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AN INVESTIGATION OF THE FAST PYROLYSIS OF CELLULOSE AND WOOD

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AN INVESTIGATION OF THE FAST PYROLYSIS OF CELLULOSE AND WOOD

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ABSTRACT

A fast pyrolysis program (Ultrapyrolysis) at the University of Western Ontario, which was initiated under the **ENFOR** program (Environment Canada/EMR), was continued and expanded under the Bioenergy Program of the National Research Council of Canada. The equipment was modified and refined to make it suitable for kinetic studies. The gas-phase kinetics for the production of total gas, carbon oxides, hydrogen, olefins and other hydrocarbons were characterized during the fast pyrolysis of cellulose and wood (i.e. poplar and red maple) feedstocks at temperatures between 650 and 900°C. The production of these major gaseous components was found to fit a first order kinetic model quite well. General insights associated with primary pyrolysis mechanisms and refinements of earlier published mechanisms were made possible by primary liquid analysis and extrapolations over time. Product distributions were found to be compatible with flash pyrolysis results from the Waterloo University (Dr. D.S. Scott) fluidized bed unit, over a wide range of temperatures. The relative importance of secondary gas-phase reactions (i.e. cracking, reforming, water-gas shift, etc.) was evaluated, and the integrity of the reactor as a valid kinetic tool was verified by a comparison of experimental ethane cracking kinetics (in the UP system) with published kinetics.

SOMMAIRE

Le programme de pyrolyse éclair (Ultrapyrolyse) de l'Université Western Ontario, mis en train en vertu du Programme de l'énergie forestière (Environnement Canada/EMR), a été prolongé et élargi et relève maintenant du Programme de bioénergie du Conseil national de recherches du Canada. On a modifié et perfectionné l'équipement afin de pouvoir l'utiliser pour des études cinétiques. La cinétique en phase gazeuse de la production totale de gaz, oxydes de carbone, hydrogène, oléfines et autres hydrocarbures, fut caractérisée pendant la pyrolyse éclair de cellulose et de bois (peuplier et érable rouge), à des températures de 650 à 900°C. On a trouvé que la production de ces principaux composants gazeux convenait bien à un modèle cinétique de premier ordre. L'analyse du liquide et des extrapolations dans le temps ont permis d'approfondir les connaissances générales des mécanismes primaires de la pyrolyse et de préciser des notes précédentes sur ces mêmes mécanismes. On a trouvé que la distributiondes produits était compatible avec les résultats des pyrolyses éclair du système à lit fluidisé de l'Université de Waterloo (Dr. D.S. Scott) pour une grande gamme de températures. On a évalué l'importance relative des réactions secondaires en phase gazeuse (c-.à -d. le craquage, le reformage, la transformation eau-gaz, etc.) et vérifié la valeur du réacteur en tant qu'outil cinétique, en comparant la cinétique expérimentale du craquage de l'éthane (dans le système UP) avec des études déjà publiées.

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1.0 INTRODUCTION

A fast pyrolysis program (Ultrapyrolysis) was initiated at the University of Western Ontario (U.W.O.) under the **ENFOR** program (Environment Canada and EMR) with the intention of engineering a steady-state process to exploit the favourable fast pyrolysis product yields which were reported in bench-scale studies. Cold modeling and "hot" reactor studies led to the development of a new ultra-rapid fluidized (URF) reactor system. Preliminary fast pyrolysis results using wood, cellulose and lignin in this system were encouraging, and are reported along with details of the design in a federal government publication [1]. The relative success of the first phase of the program led to a second phase of work sponsored by the Energy Project Office of the National Research Council of Canada (NRCC). This report presents a summary of the project objectives, literature review, system modifications and experimental work carried out during the NRCC-sponsored phase of the work. The literature review chapter is a slightly modified version of a review published in the Journal of Analytical and Applied Pyrolysis [2].

2.0 PROJECT OBJECTIVES

The primary objectives of the U.W.O. Ultrapyrolysis project funded by NRC are summarized as follows:

1. Prepare a current literature review of biomass pyrolysis with particular emphasis on the chemical pathways, kinetics, heat transfer and R & D effects associated with rapid pyrolysis studies.

2. Modify and refine the Ultrapyrolysis (UP) equipment to render it suitable for kinetic studies.

3. Enhance the operating efficiency of the UP system by improved design.

4. Investigate the vapour-phase kinetics which occur in the UP system during the fast pyrolysis of cellulose and lignin.

5. Characterize the production of valuable chemical intermediates (i.e. olefins, benzene, other unsaturates), and high quality fuel and synthesis gas (i.e. CH_4, H_2/CO) as a function of various experimental parameters (i.e. temperature, residence time, feedstock particle size, and sand thermofor loading) during the fast pyrolysis of cellulose, wood and lignin.

6. Identify the major classes of reactions which have been proposed in the literature as likely fast pyrolysis reactions, and assess their actual relative importance based on empirical results.

7. Prepare preliminary designs for a fast pyrolysis pilot plant (1 BDt/day) and a commercial prototype (100 BDt/day).

As is often the case with fundamental research programs, some of the objectives were revised (with the approval of the Scientific Authority) in response to periodic progress reviews during the course of the work. The favourable results of the cellulose kinetics experiments and the agreement of these results with the Waterloo University pyrolysis data, resulted in a greater emphasis on the pyrolysis of cellulose feedstocks (although several experiments were conducted using IEA standard poplar and red maple). The obvious lack of a defined "standard lignin" within the biomass community (and therefore the resultant questionable extrapolative and comparative value of the results) contributed to the decision to concentrate more on cellulose and IEA poplar feedstocks. The importance of the cellulose kinetics investigations and increasing cooperation with the Waterloo University flash pyrolysis research group (Dr. D.S. Scott) on mechanistic studies also resulted in a reduced emphasis on a consideration of the effects of feedstock particle size and particulate sand heat carrier (i.e. thermofor) loading. Finally, the pilot plant capacity was redefined as 10 BDt/day (vs 1 BDt/day) due to the high feedstock mass to reactor volume ratio possible on a UP reactor system. Scaling data used in the pilot design indicated that commercial prototype would likely consist of a modular reactor approach with reactor units which would likely be sized on a scale comparable to that of the pilot plant. The pilot plant design was therefore investigated in greater detail. Cost estimates for the plant were generously prepared by **Polysar** as a service to the University but had not yet been received at the time of writing of this report.

3.0 GENERAL ACCOMPLISHMENTS

Although there are a number of minor accomplishments which are natural byproducts of any fundamental research program (i.e. development of new skills, new engineering and analytical techniques, training of personnel, technology transfer, etc.), the principal unique accomplishments associated with the NRC/U.W.O. Ultrapyrolysis (UP) program may be summarized as follows:

1. Characterization of the gas-phase product kinetics of fast pyrolysis under isothermal conditions with accurate control of residence time.

2. Monitoring and "tracking" the appearance and disappearance of liquid products which appear very early in the fast pyrolysis pathway. Subsequent extrapolation permits the estimate of a crude primary product distribution resulting from the initial biomass depolymerization step.

3. Combination of independent data from Waterloo University (Dr. D.S. Scott) and the University of Western Ontario to give a congruent picture of rapid pyrolysis at moderate to high temperatures (i.e. 450 to 900°C).

4. Refinement of some earlier published speculations on the nature of the mechanism of the primary depolymerization of cellulose. These refinements were made possible in consultation with Drs. Scott (Waterloo U.), Overend (NRC) and Bergougnou (U.W.O.).

5. Speculations on the relative importance of the major secondary vapour-phase reactions which have been suggested in the literature.

6. Direct cooperation with several industrial biomass conversion projects by providing volatilization kinetics (depolymerization), reactor simulation and feasibility studies for marketable chemical intermediates.

7. Fourteen (14) "Ultrapyrolysis" papers were published during the course of the NRC project and are listed in Appendix 14.1.

4.0 LITERATURE SURVEY

The following discussion is a revised version of the literature survey which appeared in the Journal of Analytical and Applied Pyrolysis. The sections which are relevant to the Ultrapyrolysis experimental program (i.e. those sections on biomass pyrolysis and the review of fundamental research and development) have been included in their original form. However, the sections on fossil fuel pyrolysis, commercial ethylene production and fast pyrolysis gas purification have not been included in this report. The reader is referred to the published version for the complete review [2].

4.1 Fast Pyrolysis and Conventional Thermochemical Conversion

The development of a successful fast pyrolysis technology for biomass will offer a product and a process with the best features of conventional pyrolysis, flash pyrolysis, and air/oxygen gasification without many of their associated disadvantages [3-12]. Conventional biomass pyrolysis and flash pyrolysis research, which tend to maximize the production of a wide spectrum of condensibles, has clearly illustrated the need to characterize and upgrade the liquid products, and to identify viable industrial applications prior to successful commercial development [3,5-7,9,11-18].

Although several industrial product applications and proven hardware have already been demonstrated for air/oxygen gasification, some limitations with respect to product flexibility are apparent. The low-energy gas (less than 10 MJ/Nm^3) produced in air gasification is limited to close-coupled combustion-related processes and cannot be stored or transported over any significant distance due to its low energy density. Low-energy gas is not suitable as a synthesis gas precursor for methanol or gasoline, nor as a feedstock for the petrochemical industry.

Oxygen gasification yields a medium-energy gas (10-20 MJ/Nm^3) which may be economically transported over moderate distances (50-80 km) and may be used for the synthesis of methanol and ammonia, in addition to the low-energy gas uses. However, the gas product cannot directly be used as a petrochemical feedstock nor as a syngas for commercial synthetic gasoline production. Production of gasoline from medium-energy syngas requires several processing steps via the Mobil synthesis or Fischer-Tropsch pathways. Thermodynamically, the biomass or carbonaceous fuel is degraded from a very structured molecule to very simple molecules, and then reconstructed stepwise to methanol and gasoline. Available energy is lost in each step and the net process thermal efficiency is relatively low (i.e. between 40 and 45% for a wood-to-gasoline process via oxygen gasification and Mobil synthesis). It is evident that a thermochemical process which accomplishes selective pyrolysis and avoids complete degradation in the production of valuable chemical intermediates would allow a greater net process efficiency [3,5-9,13,14].

Fundamental research has demonstrated that very rapid pyrolysis of biomass and coal can be selective for the production of olefins and other valuable hydrocarbons. Four basic criteria must be met to ensure the production of adequate yields of such chemical intermediates in the development of a viable fast pyrolysis system [3,4,6-9,14,18-31]:

1. High heat transfer rates to the carbonaceous feedstock causing heat-up rates on the scale of tens of thousands of degrees celsius per second.
2. High reactor temperatures (i.e. between 600 and 1100°C).
3. Short vapour residence times (i.e. less than 500 ms).
4. Rapid quenching of the reaction products.

Successful development of the process would possess the following advantages [4,6,7,9,10,12,19,20,24,28,30,32-34]:

1. High yields of a non-condensible gaseous product (i.e. limited heavy liquid or solid by-products).
2. A relatively homogeneous gas product resulting in simpler upgrading and purification.
3. Primary product adaptability (i.e. a multiproduct facility which could produce such primary products as olefins, syngas, or SNG in response to the market demand).
4. The potential for high-quality secondary products (i.e. synthetic gasoline or a petrochemical feedstock).
5. No oxygen plant, thus improving process economics.
6. Relatively compact equipment due to fast kinetics.

This survey briefly characterizes the concept of fast pyrolysis, and relates it to conventional and flash pyrolysis. A distinction between fast and flash pyrolysis is apparent in a large portion of the literature (especially in the Canadian and European papers). Therefore, an attempt has been made to identify the criteria for this distinction in terms of the pyrolysis temperature, heating rate and nature of the final product.

A review of the proposed mechanisms and pathways of biomass pyrolysis is given; this includes solid phase pyrolysis (volatilization) and important vapour phase secondary reactions. A summary of current and past fast pyrolysis research is also included and has been divided into fundamental bench-scale work and process development (engineering) work. The fundamental work is typically concerned with characterizing the mechanisms, kinetics and chemistry of fast pyrolysis. Generally, the laboratory apparatus employed in such studies is neither suitable nor intended for scale-up to a commercial process. The process development work is designed to engineer a system or process suitable for eventual scale-up, modification, etc., for commercialization. It is not concerned with the fundamental aspects of the chemistry per se, and depends on the fundamental work as well as the existing theoretical knowledge as a design basis to be implemented using conventional or innovative engineering skills.

4.2 Pyrolysis and Fast Pyrolysis

Pyrolysis, flash pyrolysis, pyrolytic gasification, and fast (rapid) pyrolysis are terms which frequently appear in the biomass and coal thermochemical conversion literature. Pyrolysis may be defined in its broadest sense as the thermal decomposition of organic matter occurring in the absence of air or oxygen [6,10-13,17,18,35-46].

Some authors would consider oxygen-deficient (i.e. less air or oxygen than is required stoichiometrically for complete combustion) thermal decomposition to be a true pyrolysis process as long as the primary products are liquid or solid [6,11,13,17,18,35]. When the primary products of the oxygen-deficient decomposition are non-condensible fuel gases, the process is known as gasification [6,10,11,14,17,47].

Conventional pyrolysis is typically characterized by a low feedstock heating rate (less than $10^{0}C/s$), low temperatures (less than $500^{0}C$) and relatively long gas and solids residence times (i.e. greater than 5 s for the gas; solids residence times can be minutes. hours or days in duration). Tar and char are the primary products due to slow devolatilization of the feedstock, and the secondary coking and polymerization (recombination) reactions which are allowed to occur in the reactor after primary pyrolysis has taken place [6,10,11,18,39,42-44].

Flash pyrolysis is a rapid heating rate process ($10\text{-}1000^{0}C/s$) occurring at moderate temperatures (typically $400\text{-}600^{0}C$) whose liquid tar/oil products are maximized at the expense of char and gas. Vapour residence times are normally less than 2 s [6,11,12,18,41,48-51].

Fast pyrolysis is differentiated from flash pyrolysis in the biomass literature primarily with respect to temperature, vapour residence times, and end-product. Extremely high heating rates ($1000\text{-}10{,}000^{0}C/s$), high temperatures (greater than $600^{0}C$), and short vapour residence times (less than 0.5 s) are required to maximize the production of high-quality gases (i.e. olefins and other hydrocarbons) at the expense of char and condensible liquids [4-6,10-12, 17,18,22,26,29,30,39,52-58].

Pyrolytic gasification is a term applied to any anaerobic pyrolysis process, fast or slow, which gives a non-condensible synthesis gas or medium-energy fuel gas (10-20 MJ/Nm^3) as the primary product. In pyrolytic gasification, tar and char are viewed as undesirable by-products [6,17,59-61].

It is important to note that the pyrolysis terms used in this summary have been defined from a general consensus which was gleaned from an exhaustive survey of biomass literature. Terms such as "flash" and "fast" pyrolysis have been used interchangeably in some of the references [14,21,32-34,62-64]. It appears that only the one term "flash" is used in the coal literature to identify rapid pyrolysis processes which yield liquid or gaseous products and occur at moderate to high temperatures [12,65-75].

4.3 General Pyrolytic Pathways

The interest in fast pyrolysis and its potential for producing high-quality fuel and synthesis gas from biomass is due primarily to the fundamental research performed during the past two decades by Soltes and co-workers [18,45,46], Shafizadeh and co-workers [31,42-44,76], Broido [36] and Kilzer and Broido [38], Lewellen *et al*. [39], Milne and co-workers [40,55,56,77-79], Antal [3,19,20,80,91,93,122, 143] and others [12,81-84]. Their work has attempted to identify the major competitive and consecutive reactions which may occur during the thermal decomposition of biomass, and is summarized in an excellent review by the Solar Energy Research Institute [12]. Fundamental research of this nature is extremely valuable and necessary for the engineering of a viable continuous fast pyrolysis process, and therefore a short discussion on general pyrolysis mechanisms is given in the following paragraphs. Although much of the modeling is based on cellulose pyrolysis, these results appear to be consistent with those obtained in processes using wood and other biomass [3,18,80, 85,86]. A more specific discussion on the pyrolysis of ligno-cellulosic components is given in a later section.

The complex chemical mechanisms involved in pyrolysis are not completely understood, and the degradation pathway is a function of heating rate, temperature, gaseous environment, pretreatment, extent of inorganic impurities and catalysis [3,31,42,44,84,87-90]. However, a general global mechanism is presented in Figure 1, and was formulated from a consensus of pyrolysis specialists at a workshop sponsored by the Solar Energy Research Institute [12].

The reactions of primary pyrolysis are those which directly affect the solid biomass feedstock, and can be classified either as fragmentation (depolymerization) or dehydration reactions. Dehydration is dominant at lower temperatures (i.e. below 300°C), is typical of conventional pyrolysis, and involves a reduction in molecular weight, the evolution of water, carbon monoxide and carbon

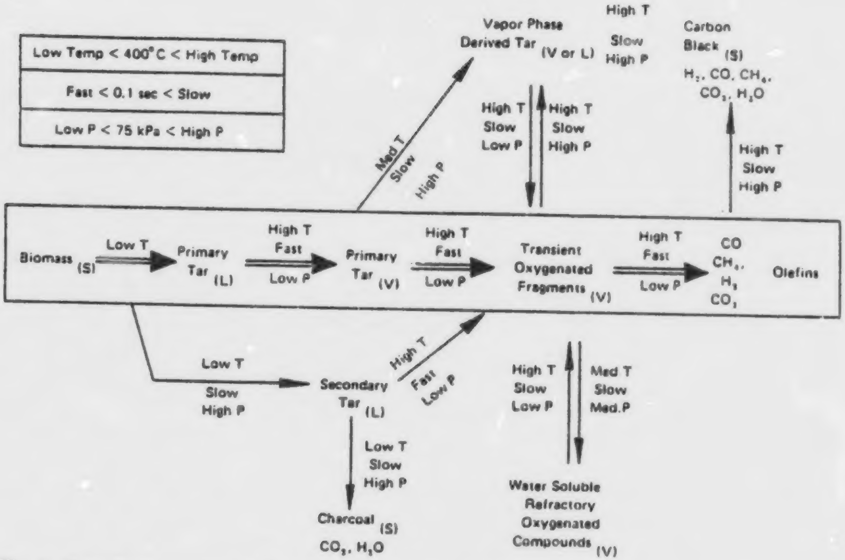


Fig. 1. Reactions competing with fast pyrolysis reactions

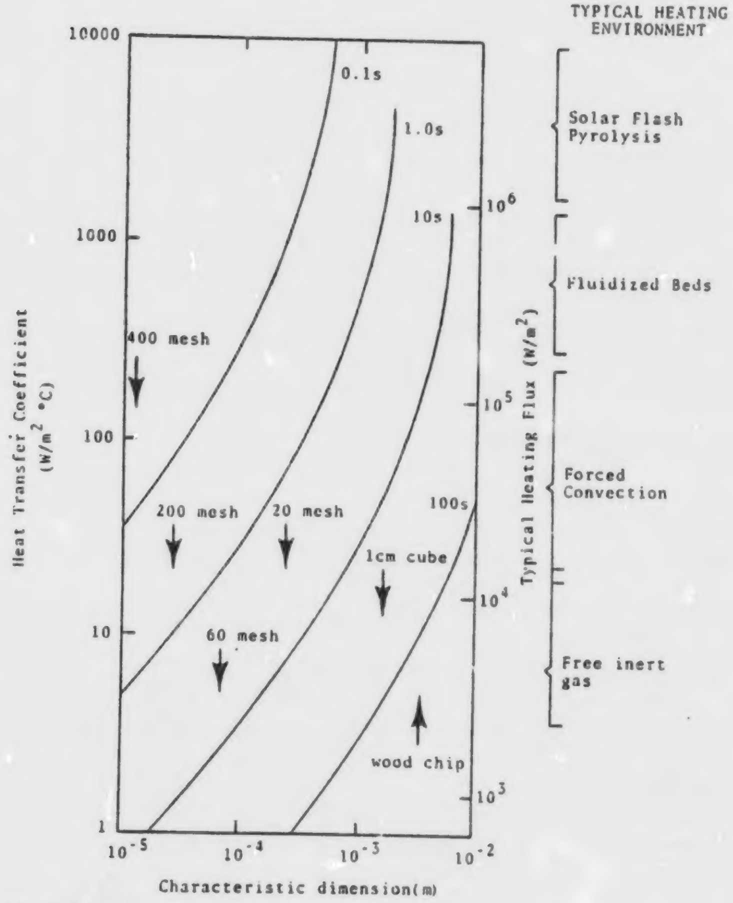


Fig. 2. Particle size and heating rates of wood.

dioxide, and the formation of char. Fragmentation predominates at higher temperatures (i.e. greater than 300°C) and involves the depolymerization of biomass to characteristic primary tar units whose nature depends on the type and composition of the biomass feed. These higher-temperature reactions are of more interest with respect to the development of a flash or fast pyrolysis process [4,6-9, 11-13,18-21,26,29,36,42-44,57,58,62,84,91,92].

The primary products of pyrolysis may repolymerize (recombine), undergo further fragmentation (cracking and reforming), or react with free-radicals. These secondary reactions must be better characterized in order to engineer a system which can selectively maximize one or more of the many possible products or intermediates, and under fast pyrolysis conditions (as defined in the previous section), they occur primarily in the vapour phase and dominate the chemistry of fast pyrolysis [12,14,26,80,93-96].

The recombination of primary products to form stable secondary tars is favoured by long vapour residence times, low to medium temperatures (i.e. 200 to 600°C) and high partial pressures. These conditions allow the primary molecules to be in close proximity for significant periods of time in the condensed phase, and permit frequent collisions to occur in the vapour phase. Extended reaction times at lower temperatures result in the formation of char, water, and carbon oxide gases from secondary tars. Elevated temperatures favour the cracking of the secondary tar to hydrocarbons, hydrogen, carbon monoxide, carbon dioxide and particulate carbon.

A pyrolytic pathway which clearly favours olefin production is illustrated in Figure 1. Once the liquid primary tar is formed on the biomass surface, high temperatures, high heating rates, and low vapour partial pressures will promote olefin formation by the following reaction sequence [12]:

1. Primary tars are vapourized from the liquid tar surface. This precludes the formation of stable secondary tars by recombination (repolymerization).
2. The vapourized primary tars are thermally cracked to produce transient oxygenated fragments. These fragments can form pyroligneous acids (i.e. acetaldehyde, methanol, furan, acetic acid, acetone, etc.) and vapour phase-derived tar by recombination under conditions which are not suitable for olefin production.
3. The transient oxygenated fragments are thermally cracked and reformed to yield olefins, other hydrocarbons, carbon oxides and hydrogen.

Extended reaction times will allow the olefins and related products to react and form particulate carbon, permanent equilibrium gases and condensible aromatic vapours. Therefore, to preserve the olefins, the pyrolysis pathway must be interrupted by rapid quenching of the intermediates before equilibrium can occur [12]. The important vapour phase reactions are more thoroughly discussed in a later section.

While there have been extensive studies of the chemical products of pyrolysis, the investigation of the physical processes accompanying pyrolysis has been somewhat neglected. This has been due in part to the close coupling of the physical and chemical processes. In the case of fire-retardant research, which has contributed significantly to the present understanding of pyrolysis mechanisms, there has not been any possibility of controlling the nature of the physical processes. For those pyrolysis processes which are intended for the production of chemical intermediates, the physical parameters such as particle size, heating rates and the nature of the heat transfer medium are all controllable process variables. Heat transfer is one of the major experimental variables exercising control over fast pyrolysis. An understanding of the nature of heat transfer is therefore implicit in the definition of "fast" and "slow" pyrolysis.

Extensive studies of the slow pyrolysis of massive samples of wood have been conducted during the course of fire research (i.e. combustion mechanisms and fire retardants). Kanury [97] attempted to describe the physics of pyrolysis and subsequently superimposed the chemical transformations on the processes of heat and mass transfer. The model included a heat flux which was external to the solid and which led to the accumulation of heat within the solid. This accumulation of heat was the result of the net inward conduction, the outward diffusion of gaseous products and the effects of local chemical enthalpy changes. The increase in thermal energy leads to depolymerization reactions and the production of smaller moieties which diffuse both inwards, ahead of the thermal wave, and outwards through the hot char layer. Radiographs of the density of cellulose cylinders show that a decomposition wave passes radially through the cylinder [97]. Radial temperature measurements show a thermal wave with plateaus suggestive of a chemical enthalpy change indicating that the wood does not behave as an inert solid from the viewpoint of thermal conduction.

Shaffer [98] analyzed the propagation of heat into massive beams under the conditions of the ASTM standard E-119 fire exposure test. Data from Maclean's [99] experiments showed that wood, under the slow heating conditions of the test, behaved as an inert solid until the 288°C wave passed through, at which point there were evidently chemical changes. Analysis of the temperature, position and time curves using the analysis equations for the movement of a plane heat source through a semi-infinite slab, yielded data on the thermal diffusivity and heat conductivity of dry wood. Tables of wood properties using measurements for temperatures much less than 100°C gave similar values. Both parameters are dependent on the humidity and density of the wood which is also anisotropic, having different values according to whether the measurements are parallel or perpendicular to the grain.

The general value of the thermal properties of wood are given as follows [98]:

ρ = density = 400-600 kg/m^3

c = heat capacity = 2.5 kJ/kg^{o}C

k = thermal conductivity = 0.1-0.2 W/m^{o}C

α = thermal diffusivity = 10^{-7} m^2/s

Using these data and neglecting the chemistry of wood pyrolysis and physical perturbations, such as the evident ablation of the outer layer of pyrolysis of wood particles in some environments, the influence of particle size and external heat transfer rates on the rate of particle heat-up have been calculated. Figure 2 shows the time taken for a particle of a given size to reach a mean temperature of half that of the heat transfer environment. The times described are only a guide in view of the gross simplification used in deriving the curves, and are likely to be over-optimistic since both endothermic reactions and the diffusion of reaction products out of the body of the particle will oppose thermal conduction into the particle.

The curves were obtained by interpolating data from Heisler charts as given in Holman [100]. The particle sizes shown are the characteristic dimension ($S = V/A$, where S = characteristic particle dimension, V = particle volume and A = particle surface area) which in the case of a sphere is one-third of the radius. Heisler charts are given in terms of two lumped dimensionless parameters known as the Biot modulus (Bi) and the Fourier modulus (Fo) which are defined as follows:

$Bi = hS/k$, where h = convective heat transfer coefficient for the bath environment

$Fo = \alpha t/S^2$. where t = time.

The Biot modulus compares the relative magnitude of the surface convection to the internal conduction resistance. The high value for wood indicates that at some limiting value of external heat transfer rate, the rate of accumulation of heat into the solid will asymptotically become constant. The Fourier modulus compares the characteristic body dimension to an approximate temperature wave penetration depth for a given time (t). Low values of α, such as that of wood and other insulators, imply very poor depth penetration at short times. Heisler charts are extremely useful in establishing which heat-up regime is operating in an experiment and are relatively easy to apply.

The isochrones of Figure 2 are for heat-up times of 0.1-100 s during which the particle mean temperature will be half that of the bath. In typical pyrolysis experiments with a bath temperature of 1000°C they cover the range from 10 to 10,000°C/s. The curves show the expected saturation with heating rate and indicate that fast pyrolysis requires heating milieus such as fluidized beds and small particles (100-1000μm). Massive particles such as wood chips can only be heated at rates of 50°C/s in fluidized beds. Obviously, techniques such as ablative pyrolysis [4,12,101-105] circumvent the restrictions implicit in Figure 2 by having solid-solid heat transfer at far higher rates coupled with abrasion of the reacting layer from the surface of the particle. Radiation heating techniques such as solar flash pyrolysis or laser irradiation show very little penetration of the thermal front when applied to massive particles for brief periods.

In order to elucidate the processes involved in pyrolysis, it would be useful if the effects of heat transfer could be separated from those of chemical reactions in the sample and from the effects of the diffusion of the reaction products away from the solid matrix. The extensive work at the Energy Laboratory at MIT has separated these by using samples corresponding to "infinite slabs" heated on both sides by grids in contact with the body. Typically, the slabs are less than or equal to 0.1 mm wide and 100 μm thick. The characteristic dimension is less than or equal to 25 μm and measured heating rates are of the order of 1000°C/s. Under such conditions the spatial inhomogeneity has been calculated to be approximately 30°C [106, 107].

For the purpose of discussion, it will be necessary to define fast pyrolysis as referring to environments and particle sizes such that it is reasonable to expect the mean rate of temperature rise to be greater than or equal to 1000°C/s, thus causing the sample to attain reasonable temperatures for reaction on a time scale corresponding to the "half life" of the reaction. A variety of sources discussed in this review show that for cellulose and other biomass pyrolysis, the reaction obeys first-order kinetics with a rate constant in the Arrhenius form having a pre-exponential factor of approximately 10^9 s^{-1} and an activation energy of the order of 120 kJ/mole. Then the half life of such a reaction is as follows:

Temperature (°C)	Half life ($t_{1/2}$)(μs)
500	90,000
800	480
1000	58

In a dynamic experiment to avoid significant temperature gradients and reaction occurrence during heat-up, clearly the half times of sample heat-up have to be less than these figures.

The global kinetics of conventional and primary rapid pyrolysis are well documented by Antal and co-workers [19,20,62,91,93,108], Shafizadeh and co-workers [31,42,44,92,109], Broido [36], Roberts [110], researchers at MIT [25,26,29,39,57,106,107], and others [11,12,58,60,81,82,85,94-96,105,111-119]. However, due to the complexity of the degradation pathway, the kinetic research has dealt primarily with the rate of solid biomass disappearance (i.e. devolatilization) rather than the rate of formation of primary, secondary and equilibrium products [25,26,31,39,41,93,108]. Since this literature survey is concerned with the rate of olefin and hydrocarbon product formation, a summary of the existing body of kinetic literature is not presented. Several good reviews have been published and should be consulted if the reader is interested in the rate of primary pyrolysis with respect to solid biomass disappearance [25,36. 39,44,57,91,108,118].

Although considerable effort has been made to experimentally determine the heat of reaction for primary and fast pyrolysis, there is a considerable range of values reported in the literature. This is probably due to variations in the biomass feedstock, experimental equipment and conditions, and the extent of the reactions which are permitted to occur in each case. There is, however, general agreement that the primary and fast pyrolysis pathways as defined in this literature review are moderately endothermic [3,11,12,14,20,33,53,58, 104,116,120-123]. Several authors report that fast pyrolysis is athermic (i.e. the heat of reaction equals zero) at approximately 700°C and increases in endothermicity with increasing temperature

[14,58,121]. Often the heat of reaction is assumed to be negligible, when compared to other heating effects, for the purpose of process design heat balance calculations [58,121]. Values between 800 and 2000 kJ/kg over the temperature range of 800-1000°C are reported for fast pyrolysis processes designed for maximum olefin yields [12,14,33, 104]. Antal and co-workers [20,108,122] have experimentally determined the heat of reaction of primary pyrolysis alone (devolatilization) to be between 100 and 400 kJ/kg in a differential scanning calorimeter apparatus at maximum temperatures of 500°C. They also observed that the endothermic nature of primary pyrolysis becomes athermic and eventually exothermic, with increasing pressure as the vapour phase polymerization and secondary char forming reactions predominate. As a rule of thumb for rough engineering calculations, some researchers suggest that 10% of the heat of combustion of the biomass feedstock gives an adequate estimate of the heat of fast pyrolysis [3,12,53,121].

4.4 Primary Pyrolysis of Lignocellulosic Components

It was previously assumed that the pyrolysis of a given biomass material was simply the sum of the pyrolytic properties of its individual components. Presently there is general agreement that the sum is very similar but not identical to the whole biomass pyrolysis, and that synergistic effects are evident [3,18,26,31,56,80,81,85,86. 93,123]. For secondary pyrolysis, where cracking of the primary tars is severe, Antal [13] reports that, regardless of the nature of the biomass component, the products are "normalized" and the gas product distribution is practically identical. In this case it is suggested that the properties of the whole biomass material in severe fast pyrolysis are similar to each of the components.

In any event, it is clear that a study of the pyrolysis of individual cellulose, hemicellulose and lignin compounds will be of considerable use in predicting the behaviour of a given biomass material of known lignocellulosic composition. In this section the three major biomass constituents are identified and characterized with respect to chemical structure and primary pyrolytic behaviour.

Cellulose, the principal cell wall component in biomass tissues, is a polymer of anhydroglucose units ($C_6H_{10}O_5$) connected to each other by ether-type linkages known as glucosidic bonds. It is characterized by an orderly crystalline structure (Figure 3) and constitutes between 40 and 50% by mass of most dry woods. Aside from the secondary hydrogen bonds and Van der Waals forces between the cellulosic strands, the weakest bonds within the chain are the C-O glycosidic linkages [3,11,26,31].

All other polymeric polysaccharides in biomass tissues are known collectively as hemicellulose, and constitute between 25 and 35% of the dry mass of most woods. Hemicellulose is a complex heteropolymer which exhibits a branched molecular structure, shows significant variation in composition among species, and contains two to four (and occasionally five to six) different simple sugar units [3,11,26]. Included among these units are D-xylose, D-mannose, D-glucose, D-

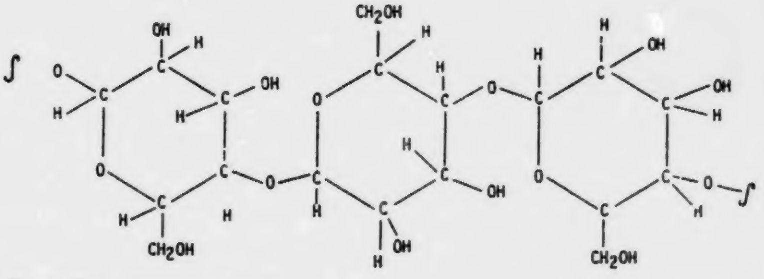
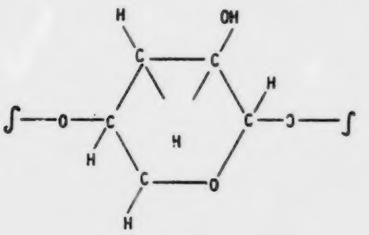
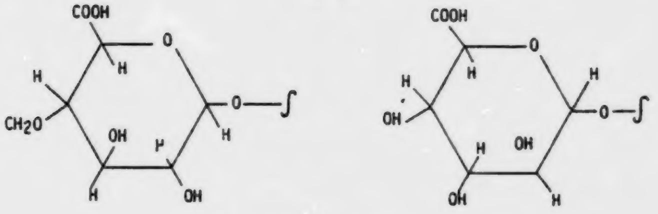


Fig. 3. The cellulose molecule



Xylan



Acid Xylans-Terminal Groups

Fig. 4. Xylan hemicellulose strucutre

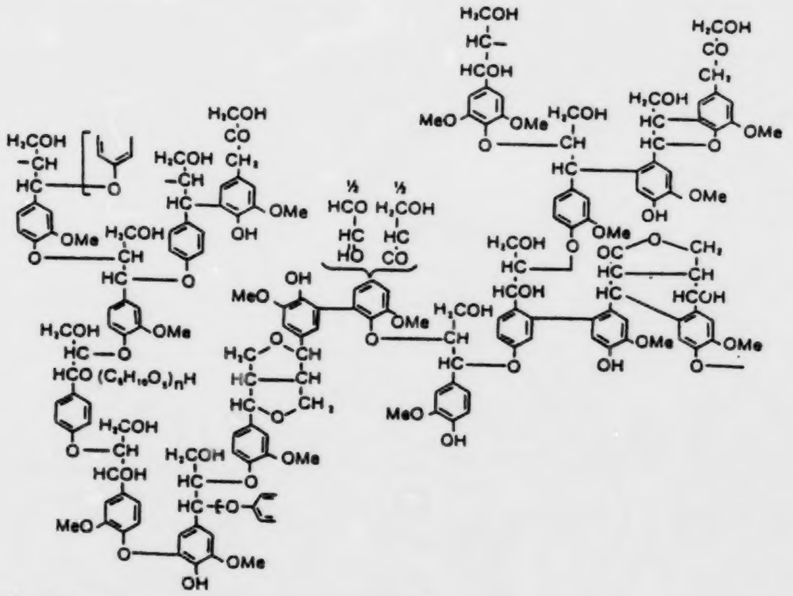


Fig. 5. Representative structure of coniferous lignin

galactose, L-arabinose, etc. Xylan, often termed pentosan, is the predominant hemicellulose in wood and is a polymer of the pentosan sugar xylose. Some typical xylans are shown in Figure 4.

The third major biomass component, termed lignin, is an extremely complex non-carbohydrate polymer based primarily on the phenylpropane unit, and constitutes between 15 and 30% by mass of most wood species [3,11,26,125]. It acts as a cementing agent for the cellulose and hemicellulose fibers, and is composed of several phenylpropane monomer groups which form the polymer by a variety of linkages involving the aromatic rings and functional groups (Figure 5).

Of all lignocellulosic components, the thermal decomposition of cellulose has been best characterized and is generally thought to proceed by two major competitive reaction pathways [3,11,31,35,38,39, 42,44,76,80,81,84,88,91,108,112,122,124,126,127]. Cellulose dehydration reactions are dominant at temperatures below 300°C and result in a reduction in molecular weight by bond scission, the appearance of free-radicals, the elimination of water, the appearance of active carboxyl, carbonyl and hydroperoxide groups, and the production of carbon oxide gases and char [11,18,31,35,38,42,44,80,91,108, 109,112,122,126]. The yields of each product are thought to be a function of final temperature, heating rate and residence time. The reduced molecular weight solid substrate which is formed after bond scission, and which precedes and accompanies char formation, is often referred to as dehydrocellulose or anhydrocellulose [18,38,51, 108,112,122]. The dehydration pathway is of little interest for the production of light volatiles and hydrocarbons, and is thoroughly characterized elsewhere in the literature [38,44,76,112].

The second major degradation pathway, known as depolymerization or fragmentation, competes significantly with dehydration at approximately 300°C and rapidly predominates as the temperature is increased [11,18,35,38,39,42,44,76,80,91,108,109,122,124,126,127]. Depolymerization of cellulose is accomplished by transglycosylation, which is a rapid cleavage of the glycosidic bond accompanied by free hydroxyl group substitution, and results primarily in the production of the characteristic monomer tar unit, levoglucosan. Levoglucosan and other less abundant primary tars, which are illustrated in Figure 6, may undergo secondary vapour phase reactions resulting in repolymerization to stable heavy tars or cracking to lighter fragments and carbon black. Evaporation of the primary tars from the solid surface is highly endothermic. Therefore, an increase in reactor temperature may increase the rate of primary product evolution without an increase in the solid biomass surface temperature. Antal [80] speculates that it should be possible to obtain two molecules of ethylene from the secondary cracking of a levoglucosan molecule. This is equivalent to a 35% mass yield of ethylene from cellulose.

Hemicellulose, whose decomposition is initiated as low as 120°C and is completed by 325°C, is the most reactive of the three major biomass components [3,11,82,84,94,112]. A degradation pathway similar to that of cellulose is proposed in that dehydration reactions are important at temperatures less than 280°C and are replaced by rapid

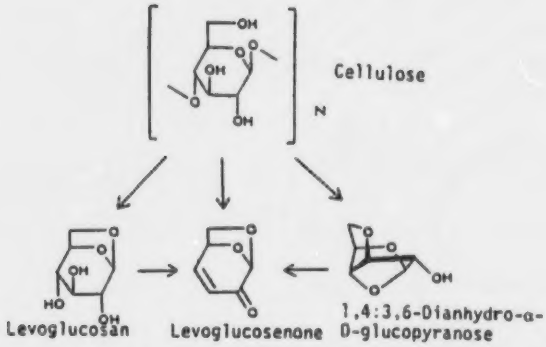


Fig. 6. Levoglucosan and related primary tars

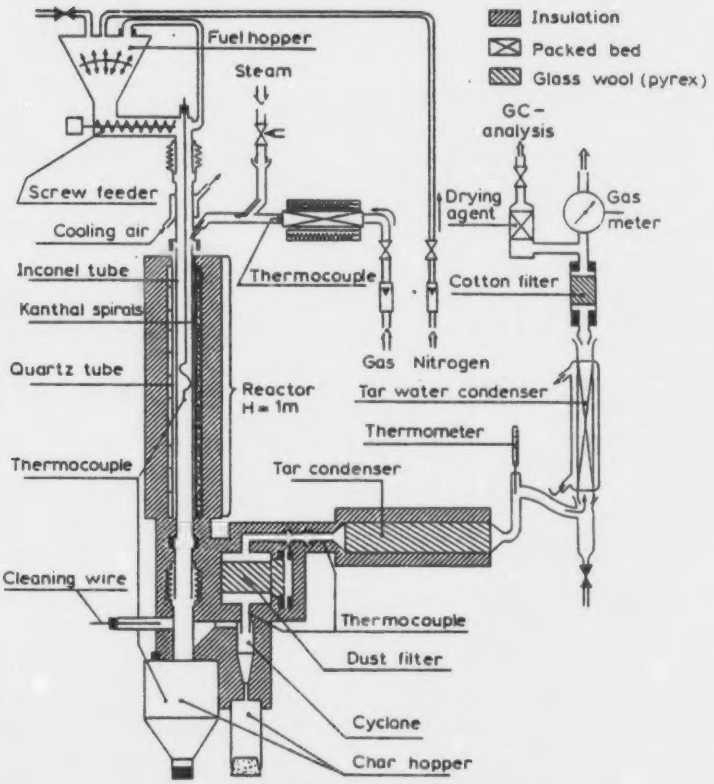


Fig. 7. Royal Institute experimental fast pyrolysis apparatus

depolymerization as the temperature is increased [112,124]. Dehydration is characterized by random cleavage of the C-O bonds producing branched-chain anhydride fragments, water-soluble acids, char and light gases [3,81,112,124].

In the case of high-temperature depolymerization, a characteristic tarry intermediate (i.e. the analogue of levoglucosan in cellulose pyrolysis) is assumed to exist from kinetic data, and is thought to be furan or furfural for hemicellulosic pentosans, but has not been clearly identified [3,80,81,84]. These furan derivatives are difficult to isolate due to their extremely rapid formation and decomposition. The secondary high-temperature products from hemicellulose rapid pyrolysis are similar to those of cellulose [80, 124].

The mechanism and kinetics of the primary pyrolysis of lignin have not been as extensively investigated as those of cellulose pyrolysis, and a major characteristic primary pyrolysis product has not been identified [3,11,80,81,112,124]. However, recent lignin results using direct mass spectrometry show a series of methoxy phenols as predominant primary pyrolysis products [56]. This lack of a clear understanding can be directly attributed to the complex structure of lignin which varies significantly as a function of species and method of preparation. In general, lignin is more thermally stable than other components, and under similar conditions produces more char and a higher fraction of aromatics in the liquid product than does cellulose or hemicellulose [31,57,81,82,84,94,112,124]. It has been proposed that primary pyrolysis occurs with the cleavage of the straight carbon chains which connect the aromatic units. Antal [80] speculates that rapid pyrolysis may initially result in the formation of monomeric phenylpropane units (which are joined by ether linkages), patterning to some extent the depolymerization of cellulose by the cleavage of the glycosidic bond. Further pyrolysis gives rise to phenols, cresols, catechols, xylenols, etc. and char from aromatic monomers, and produces carbon oxides, hydrocarbons, aqueous acids and char from the straight carbon chain [81]. Fast pyrolysis lignin studies are also being conducted at the University of Washington [23,24,128] and the Massachusetts Institute of Technology [129], and are reviewed in the discussion of fundamental research.

Shafizadeh and Chin [124] summarize the primary depolymerization of the three major wood components as follows:

1. Hemicellulose is the most reactive component and depolymerizes between 225 and 325°C.
2. Lignin is the most thermally stable component and decomposes gradually between 250 and 500°C.
3. Cellulose is intermediate in terms of its reactivity and decomposes between 325 and 375°C (depolymerization is initiated at a higher temperature than lignin but occurs rapidly within a much narrower range).

4.5 Secondary Reactions

If allowed to take its course, pyrolysis occurs via two distinct sequential steps which are largely independent of one another [3,80, 96,130]. The first step which involves the primary solid phase reactions (depolymerization or dehydration) is practically instantaneous in flash and fast pyrolysis processes (i.e. the chemical kinetics are extremely fast and are generally not limiting unless particles are less than several hundred microns in any single characteristic dimension). The second step includes the secondary reactions which occur in the vapour phase (or at least involve vapour phase components reacting with char or carbon black), is limited by chemical kinetics, and dominates the chemistry of pyrolysis [3,19,31,80].

Five general secondary reactions are known to be significant in conventional pyrolysis and gasification, and must be evaluated with respect to their relative significance in fast pyrolysis processes. These reactions include cracking, reforming, the water-gas shift, the Boudouard reaction and the carbon-steam reaction.

The thermal decomposition or vapour phase pyrolysis of heavy hydrocarbons to smaller fragments is known as cracking. During the course of this endothermic reaction, carbon-carbon, carbon-hydrogen and carbon-oxygen bonds are broken or rearranged resulting in shorter carbon chains, ring cleavage, the production of hydrogen and carbon oxides, and the formation of unsaturated compounds (olefins and alkynes). Although it has not been fully characterized with respect to its specific chemical pathway in biomass pyrolysis, vapour phase cracking is recognized as the single most important secondary reaction in fast pyrolysis and occurs on a time scale of tens of milliseconds at temperatures exceeding 700°C [3,12,18-20,26,29,79,80,95,96,104,113,131-133]. As was outlined in the discussion on general pyrolytic pathways, the final product distribution depends on residence time and temperature. High yields of valuable hydrocarbon intermediates, which are not predicted by chemical equilibrium, can be realized. Nunn et al. [24], Antal [20,93] and Graham et al. [2,6,7,9,28] have concluded that the major products of the initial cracking of biomass "liquids" are carbon monoxide, methane, hydrogen and ethylene at temperatures between 750 and 1000°C. Other hydrocarbons are also formed but are rapidly cracked at these temperatures, and persist only in small quantities. Carbon dioxide and water production are thought to be products of primary pyrolysis along with the primary vapours and some initial molecular hydrogen formation. Antal [93] further speculates that a fixed fraction of carbon atoms appear to be dedicated to CO formation from biomass-derived volatile matter at temperatures above 600°C. The promotion of decarboxylation and dehydration reactions would favour olefin production and would be accompanied by a decrease in CO formation and an increase in CO_2 evolution. Antal [93] reports, however, that the role of decarboxylation is decreased as the temperature is increased, and that some means must be found to access those carbon atoms dedicated to CO formation if a dramatic increase in ethylene yields is to be realized.

Reforming is a broad class of endothermic reactions of hydrocarbons with steam at elevated pressures which results in isomerization, hydrogenation and eventual fragmentation to light hydrocarbon and hydrogen free-radicals. These reactions have been assumed to occur at a significant level in the pyrolysis vapour phase [3,19,96, 130]. It has been clearly demonstrated, however, that at the temperatures, residence times, and relatively low pressures characterized by fast pyrolysis, reforming is completely eclipsed by the dominance of the cracking reactions [20,32,130,133].

The water-gas shift is the reversible reaction of steam with carbon monoxide to produce hydrogen and carbon dioxide. This exothermic reaction is considerably faster than the reactions of carbon-steam and carbon-carbon dioxide [95,96,114,120], and may contribute to the final product distribution in fast pyrolysis processes [95,133]. The vapour phase temperature and nature of the carrier gas (i.e. steam, carbon dioxide, recycle gas, etc.) will determine the direction and extent of the reaction. In the absence of an appropriate shift catalyst such as iron or nickel, the forward step (i.e. the production of hydrogen and carbon dioxide from steam and carbon monoxide) is faster than the reverse step at temperatures below 810°C [133]. Over the entire fast pyrolysis temperature range an approach to equilibrium clearly favours the production of steam and carbon monoxide at the expense of hydrogen and carbon dioxide [134].

The carbon-steam and carbon-carbon dioxide (Boudouard) reaction are similar with respect to rate, mechanism and degree of endothermicity. The former is the reaction of carbon with steam to produce hydrogen and carbon monoxide, proceeds at a negligible rate below 830°C, and is thought to play a minor role in fast pyrolysis due to its relatively slow kinetics (i.e. compared to primary pyrolysis and cracking) at temperatures exceeding 830°C [3,20,93,96,104,130,135]. Nandi and Onischak [117] report the kinetics on a minute time scale in the temperature range of 630-930°C, and Hallen et al. [135] conclude that only by catalysis can the carbon-steam reaction participate significantly in the pyrolysis process.

The Boudouard reaction which is that of carbon with carbon dioxide to produce carbon monoxide, is hardly detectable below 850°C and is also thought to play only a minor role in fast pyrolysis [3,80,93,95, 115,120]. Edrich et al. [115] report that its rate may be up to 100 times slower than that of primary pyrolysis at temperatures approaching 1100°C. In his initial work, Antal [80] treated biomass as a carbon source for the Boudouard or steam reactions but quickly recognized the predominance of the pyrolytic phenomenon.

It is apparent from the discussion of important secondary reactions that aside from the water-gas shift at temperatures less than 810°C, steam is a relatively inert participant in fast pyrolysis processes. The majority of researchers have confirmed that under typical fast pyrolysis conditions, steam acts primarily as a diluent to prevent secondary polymerization and promote cracking in the vapour phase [80,93,104,130,136]. It is therefore evident that if carbon is formed in the primary reactions, it will persist through the secondary reactions and appear in the final product distribution.

It is important to note that in spite of the preceding discussion, the secondary pyrolytic reactions have not been thoroughly characterized (especially with respect to the free-radical chemistry). Antal [3] emphasizes this point in a report to the Congress of the

United States where he notes that the state of the art of biomass pyrolysis is "roughly comparable to that achieved one half century ago by the hydrocarbon processing industry in the steam cracking of alkanes to olefins".

4.6 Fundamental Fast Pyrolysis Research

The research reviewed in this section includes the laboratory bench-scale studies which are concerned primarily with the characterization of the chemistry, mechanisms and kinetics of the fast pyrolysis of biomass. The equipment used is not suitable nor intended for eventual commercial scale-up. In general, experimental work has demonstrated that little or no char need be formed during the fast pyrolysis of biomass [3,4,6,7,9,10,14,19,20,26-30,32-45,49,50,81, 91,105,114,137] and that olefin yields of 10-15% by mass of the biomass feedstock can be realized [3,4,7,9,12,104,138,139].

There is also a general consensus that for conventional slow pyrolysis of relatively large particles, the primary reactions are heat transfer-controlled and are not limited by pyrolytic chemical kinetics [3,19,31,44,58,81,91,96,114,119,140,141]. Although several authors have speculated that the primary reactions of fast pyrolysis are also heat transfer-controlled (i.e. the reaction rates are faster than the heat transfer rates which define fast pyrolysis) even for extremely small particles, researchers at the Massachusetts Institute of Technology [29,106,107] have experimentally demonstrated that this is not true for all cases. They reported that the conversion of thin

(100 μm) strips of cellulose decreased as the heating rate was increased from 100 to 10,000°C/s for a series of constant peak temperatures between 400 and 1000°C. In effect, at lower heating rates more time was made available for conversion to proceed during heat-up of the sample. For these experimental conditions, the reactions were clearly chemically controlled. However, as the characteristic sample dimension becomes larger, heat transfer control will become important and eventually limiting.

Although the above discussion implies that it is not the heating rate but rather the time made available upon reaching the final temperature which enhances conversion, this does not mean that the heating rate is insignificant in the production of valuable chemical intermediates. In fact, the rapid heating rate is required to quickly bring the sample to the desired reaction temperature before an undesirable pyrolytic pathway has been followed [12].

Recent research by Milne and co-workers [40,55,56,77,78,131] in a molecular beam mass spectrometer apparatus has generally confirmed the fast pyrolysis mechanism outlined in Figure 1. Real time sampling, precise control of vapour residence times, and the development of an excellent adiabatic expansion technique to quickly (microseconds) freeze intermediate products has permitted the observation of the evolution of the primary tars (i.e. anhydroglucose units, levoglucosan, etc.), transient oxygenated fragments and olefins as a function of time. Preliminary results indicate that the "olefin window" (i.e. a time interval after primary pyrolysis during which maximum yields of olefins are apparent) occurs between 30 and 150 ms after the primary tars vapourize from the liquid surface of the pyrolyzing biomass at 900°C.

Fast pyrolysis research sponsored by Crown Zellerbach [138] has shown that ethylene is favoured at vapour phase temperatures of 700-900°C, while acetylene is favoured in the range of 1200-1500°C. Mixtures of various proportions occur between 900 and 1200°C. While the majority of experiments were conducted in an induction furnace at temperatures above 1000°C, some were carried out in plasma arc and electrical resistance ovens. Residence times varied between 0.1 ms and 2 s. Ethylene yields approaching 15% of the dry wood feedstock were achieved in the batch-mode bench-scale apparatus. Calculations predicted a 40% theoretical yield, and a 25% yield was assumed to be reasonable for a continuous commercial scale process.

Systematic studies of the effects of temperature (300-1100°C), solids residence time (0-30 s) and heating rate (less than 100 to 15,000°C/s) on the yields, composition and rates of formation of products from the rapid pyroloysis of small samples of wood, cellulose and lignin were performed at the Massachusetts Institute of Technology [25,26,29,57]. Biomass samples weighing approximately 100 mg were enclosed in a folded strip of 325-mesh stainless-steel screen wired into an electrical circuit. Temperature and residence time were found to be the most important reaction conditions in fast pyrolysis, while the heating rates were thought to be explicable in terms of their influence on these two parameters. The overall weight loss (i.e.

degree of volatilization) achieved from wood, cellulose and lignin was 93, 97 and 86%, respectively. Char yields decreased with increasing temperatures to a minimum of 3% by mass at 800°C and at shortest solid residence times. Maximum yields of ethylene occurred between 800 and 1000°C. Accurate estimates of vapour/gas residence times were not reported.

Fast pyrolysis of sawdust samples (100-300 mg; 25-400 µm) and wood chips (30 mm x 18 mm x 2.5 mm) was conducted at the University of Nancy (France) in a free falling system consisting of a vertical quartz tube in an electrical furnace with a temperature range of 500-1000°C [33,53,140,142]. The heating rate and the vapour residence time were not varied but were estimated to be 1000°C/s and less than 1 s, respectively. The char yield was consistently high and decreased with increasing temperature to a minimum of approximately 25% (by mass) at 800°C. It is assumed that secondary reactions and low-temperature carbonization was allowed to occur due to the insulating effect of the pyrolyzing chip surface or outer particles (i.e. those farthest from the reactor axis). Ethylene yields were significant between 700 and 900°C with a maximum at 750°C.

A down-flow quartz tube reactor housed in an electrical resistance oven was also used for fast pyrolysis studies at the Swedish Royal Institute of Technology [32,34] and is depicted schematically in Figure 7. The heating rate for the particulate wood sample (400-500 µm) trials was fixed, and was estimated to be 1000°C/s. Solids residence time was varied from 0.4 to 1.2 s. Char yields decreased

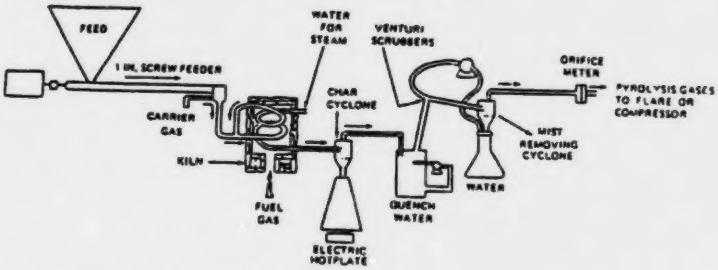


Fig. 8. China Lake entrained tubular pyrolysis apparatus

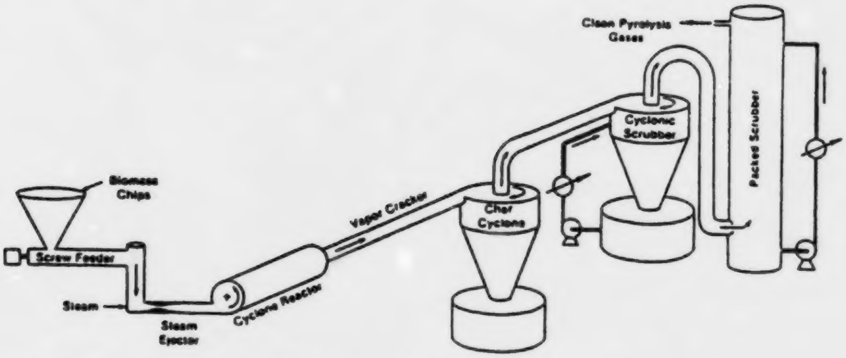


Fig. 9. SERI modified entrained flow ablative—pyrolysis schematic

with increasing temperatures levelling off to a minimum of approximately 10% by mass at temperatures exceeding 650°C. Ethylene yields were significant between 700 and 950°C, with a maximum production at 800°C. Secondary thermal cracking of the primary fast pyrolysis volatiles significantly enhanced the yields of ethylene and methane, favouring ethylene at cracking temperatures exceeding 700°C.

Some interesting work using microwave techniques to study biomass fast pyrolysis has been carried out at the University of Washington [23,24,128]. Although final feedstock temperatures and vapour residence times are not reported, heating rates at the biomass surface were estimated to be between 10 and 20°C/s. Solid char residues were found to be 2.9, 9.2 and 39.8% by mass for cellulose, wood (red alder) and lignin (Indulin AT), respectively. Corresponding percent yields of acetylene and ethylene, respectively, were 7.7 and 3.0 for cellulose, 4.4 and 0.8 for wood, and 4.6 and 0.7 for lignin.

Two studies at the Ames Research Center, NASA [137] and the Colorado School of Mines [139] were designed primarily to study the effect of heating rate on fast pyrolysis. The Ames program employed an electrical resistance furnace, carbon arc, xenon flashtube and laser heat sources to achieve increasing heat rates for cellulose fast pyrolysis. Laser pyrolysis with an exposure time of 0.4 ms and surface temperature exceeding 600°C resulted in 100% conversion to gases (i.e. no tar, nor char produced). The Colorado researchers used a PYROPROBE unit to study the pyrolysis of wood particles (5 mg; less than 125 μm) at 1000°C and filament heating rates between 250 and

40,000°C/s. The highest heating rates gave the highest ethylene mass yields of approximately 15% of the wood feedstock. Both studies conclude that the rate of heating of biomass makes a profound difference in the yield and composition of pyrolysis products, and on the reaction path followed.

Other fundamental fast pyrolysis studies of biomass have employed concentrated solar energy [13,19,20,33,62,80,88,143] and more standard thermogravimetric (TGA) techniques [82,83,89,90,93,108,120,124,127, 144,145] to supply heat to the feedstocks. Fluidized bed [49-51,111] and vacuum pyrolysis [42,44,81,84,86,91,108,109,124,126,127,132] equipment has been used to study the rates, mechanisms and chemistry of primary pyrolysis where liquid products predominate.

4.7 Process Development Work

The research reviewed in this section consists of those studies designed to engineer a process concept, and hardware, which may eventually be modified or directly scaled up to form the basis of a commercial process. It is not primarily concerned with the exploration of the fundamental chemistry and mechanisms of fast pyrolysis, but utilizes available empirical data and conventional or innovative engineering skills.

A widely publicized system is based on the China Lake entrained flow pyrolyzer [8,15,22,146-148] which subsequently gave rise to the

SERI fast ablative pyrolyzer [4,101-105] when principal researchers transferred from the China Lake facility to that of the Solar Energy Research Institute (SERI). The China Lake apparatus is illustrated in Figure 8, and consisted of a Vibra Screw feeder, a CO_2/steam injector, a coil tube heater housed in a propane-fired kiln, a char cyclone and a quenching/condensing train. Although the vast majority of the trials were carried out using a 250-μm free flowing municipal solid waste fuel known as ECO-II, wood flour (less than 180 μm) and Avicel pH 102 cellulose (100 μm) were also fast pyrolyzed at 750°C for approximately 150 s. Maximum yields of ethylene were 9.3 and 8.6% by mass for cellulose and wood, respectively. Less than 0.03% of the input wood remained as a char residue and the cellulose char residue was negligible (less than 0.001%). A gas processing train, which is described in a later section, was incorporated for purification and polymerization of the product.

The SERI fast-ablative entrained flow pyrolyzer is illustrated in Figure 9. The heart of the process is the cyclonic reactor, whose heated walls are designed to preferentially transfer heat to the entrained solids rather than to the entraining gases. The biomass feedstock, whose particle size is less than 10 mm, enters the reactor tangentially and is centrifuged to the red-hot wall. Heat is transferred by solid convective heat transfer to the biomass, and causes vapourization of the primary pyrolysis tars which are carried quickly from the reactor in a high-velocity steam carrier gas. The tar vapour design residence time in the cyclonic reactor is between 75 and 175 ms with exit temperatures of 500 to 600°C. The dilute vapours are cracked in the thermal vapour cracker tube for 70 to 150 ms (also a design estimate) during which time the temperature is raised to between 700 and 1000°C. The cyclone wall temperature is typically 1000°C. After preliminary shakedown, a recycle loop and cyclone were added to reinject unpyrolyzed biomass (when required) and a helical coil was installed inside the reactor to extend the solid residence time by reducing the natural pitch of the spiral path of the particles. Although heat is currently supplied to the reactor by thermal radiation from electrical resistance heaters, the use of condensing sodium vapours at 700-900°C is being considered in order to enhance the heat flux to the biomass through the reactor wall.

Preliminary testing has been carried out at wood feed rates between 3 and 23 kg/h, residence times between 400 and 1100 ms, temperatures of 500-750°C, and steam-to-biomass ratios of 1:5. Ethylene and total hydrocarbon non-condensible gas yields of 6.1 and 16.8% by mass of the feed, respectively, are reported. In general, particle size studies in the SERI unit show very similar results over the range 0.18-5 mm with slight reductions in ethylene and total hydrocarbon yields with increasing size. The effect of the reaction temperature history of the primary tar vapours is reported to be much more important with respect to the extent of gasification and to the olefin yields than the steam-to-biomass ratio. Steam is, therefore, assumed to act only as an inert carrier except when present in sufficiently large amounts to alter the temperature history (and therefore the extent of cracking and olefin yields).

Although the Ultrapyrolysis process at the University of Western Ontario [1,6,7,21,27,28,149,150] has demonstrated its utility for fundamental kinetic studies, its basic configuration (i.e. a steady-state flow reactor system), and mass flowrate capacity qualify it as process development work. This process will be characterized in greater detail in a later chapter.

A cyclonic type reactor is also being researched in Nancy, France by the combined efforts of the University of Nancy and the Chemical Engineering Science Laboratory [63,121,129,151]. Researchers are presently concentrating on the flow patterns, particle residence times, heat transfer between the heated walls and carrier gas/solid particles, and the nature of products obtained in an electrically heated cyclone. It is intended that the first continuous system will use solar energy as the heat source for pyrolysis. Preliminary work, sponsored by the Chemical Engineering Science Laboratory (Nancy, France) and Princeton University, has been completed using solar energy for the fast pyrolysis of various biomass feedstocks at the Odeillo 1-MW solar furnace in Odeillo, France [19,62,80]. Char yields were low, being 1-4% (by mass) for all of the wood, cellulose, lignin and corn cob biomass feedstocks used in the study. Permanent gas yields were also low, (i.e. 13-31% of the cellulose by mass) due to the relatively low gas phase temperatures which quenched the primary tar products as they vapourized from the hot solid surface. Heating rates in the range of 10,000-100,000°C/s were reported.

Other biomass fast pyrolysis process designs have incorporated single fluidized beds [58,141], twin fluidized beds [48,52,130], entrained beds [64,130,152,153], single vessel circulating beds [154], molten lead baths [155] and atomized suspension techniques [16,59,156] for the rapid pyrolysis of various biomass materials. Novel reactor systems currently being developed for the thermal cracking and fast pyrolysis of solid and liquid fossil fuels deserve consideration for applications to biomass processing. Some of these systems are utilizing solid heat carriers (char or inerts), unique fast solids mixers, and rapid quenching methods to achieve the rapid heat transfer and short residence times which are required for biomass fast pyrolysis process development [92,129,157,158].

5.0 ULTRAPYROLYSIS SYSTEM MODIFICATIONS AND REFINEMENTS

The primary objective of the initial Ultrapyrolysis project (sponsored by **Enfor**) was to engineer a steady-state process which would successfully demonstrate the chemistry of fast pyrolysis. This demonstration resulted in the production of valuable non-equilibrium thermochemical conversion products (olefins, benzene and reactive intermediates) and synthesis gas (carbon monoxide/hydrogen) in equipment that could be used as a conceptual basis for eventual commercial scale-up. The heart of this primary objective was the development of a new reactor design in order to exploit fast pyrolysis product yields. The project was a technical success and preliminary results were encouraging, but there was no attempt to systematically study and characterize the chemistry and kinetics of fast pyrolysis. This systematic work was sponsored over the past three years under the **NRC Bioenergy** program, and required several system modifications and refinements in order to generate reliable kinetic and process optimization data.

Upon completion of the first phase of the project, the fast pyrolysis system was dismantled, modified and reinstalled in a larger laboratory. Modifications were made to improve the efficiency of operation, to remove inherent operational problems, to reduce the system pressure drop, to prepare for kinetic studies and, finally, to enhance liquid product recovery.

Construction of a centralized control panel with a flow diagram and enunciators was the major factor in improving the efficiency of operation. The controller is thus able to respond quickly to system upsets and to monitor steady-state parameters more effectively. Replacement of the fluidized bed thermofor (i.e. heat carrying solids) and biomass feeders with custom-made mechanical feeders reduced the occurrence of transport line plugging and vastly improved the constancy of feed rates. In addition, the new feeders were easier to set, monitor and operate. Several components of the biomass feeder were constructed of lighter materials (i.e. plexiglass vs. steel) allowing direct installation on an electronic balance. This facilitates accurate monitoring of the biomass flow-rate and enhances the determination of the mass balance. The use of plexiglass was made possible by a reduction in the system operating pressure.

The system pressure drop was greatly reduced (by an order of magnitude) with the use of larger tubing in the construction of a new preheater coil and transport lines. A secondary advantage in the use of large transport lines was a reduction in line plugging. The system was reinstalled in a multi-level tower area so that the flow of solids and gases would always be in a downward direction. An additional reduction in system pressure drop was thus gained through the effects of gravity.

The use of a stream of cold particulate solids (i.e. Cryofor) to rapidly quench the reaction products was replaced by a cryogenic nitrogen stream. This enhanced product recovery and simplified system operation by the removal of the fluidized bed solids feeder and its complicated control system. Approximately twenty hot experiments were conducted to test the operability and integration of the new components of the modified pyrolysis system.

In preparation for kinetic studies, thermocouples were installed along the reactor length to monitor the isothermal operation. Isothermal operation was effected by converting the reactor oven from a single zone to a two zone unit, by adding and sealing insulative layers (i.e. this simultaneously improves the thermal resistance and reduces convection in the tubular ovens) and by adding local heating cables within the insulative layer of the injectors. These heaters known as "MI" (i.e. mineral insulated) Cable, can operate up to 1100°C and consist of an Inconel sheath surrounding a nichrome wire packed with magnesium oxide.

Active and precise control of the residence time is necessary for kinetic studies but was not possible in the original equipment (i.e. the residence time was fixed by constant reactor dimensions for a given set of system parameters). In order to allow effective control over the residence time for kinetic studies, a number of stainless steel tubular inserts were fabricated which could reduce the volume of the reactor in a stepwise fashion. These inserts coupled with the large reduction in operating pressure allowed for the selection of residence times between 50 and 900 milliseconds over a broad temperature range (650-900°C). More than one hundred (100) hot experiments were conducted to test and monitor the modifications relating to kinetic studies. These experiments were completed when consistent, reliable and reproducible operation was demonstrated.

The recovery of liquid products (i.e. condensibles) was enhanced by the design, construction and integration of the following units:

1. An efficient cyclonic condenser immersed in a cold water bath replacing the coiled tube condenser/heat exchanger.
2. An electrostatic precipitator which extended the run time of a low temperature or short residence time experiment by reducing the load on the filter (thus keeping the pressure drop low for an extended period of time).
3. A larger porous metal filter cartridge with a lower mean pore size than the original (i.e. 0.2 μm vs 5.0 μm) and a larger surface area (by a factor of 3.5).

A summary of the designs of the cyclonic condenser and the electrostatic precipitator are given in Appendix 14.2.

6.0 CURRENT ULTRAPYROLYSIS FLOW SCHEME

The major components of the current Ultrapyrolysis (UP) process are illustrated in Figure 10. Rapid mixing and heat transfer are carried out in two conical vessels known as vortical contactors or Vortactors. The first has been termed a Thermovortactor and allows heat to be transferred from a hot "thermofor" stream (i.e. gaseous nitrogen, suspended particulate solids, or a combination of the two) to the biomass. The second is a Cryovortactor and allows fast quenching of the products by the direct transfer of heat to "cryofor" (i.e. cryogenic nitrogen). The Thermovortactor has two opposing tangential inlets for the thermofor. One tangential stream effectively destroys the momemtum of the other causing severe turbulence. Biomass feedstocks are then injected from the top of the Thermovortactor through an air cooled tube into the turbulent region where mixing occurs within 30 milliseconds. The hot gaseous product is rapidly cooled (i.e. in less than 30 ms) by the injection of a single tangential stream of cryogenic nitrogen.

Mechanical table feeders are used to supply biomass and thermofor solids to the reactor system. Solids pass from sealed hoppers (which have a sufficient inventory of solids for several experiments) through a double funnel system and are thereby metered onto a rotating table. Two fixed armatures sit near the surface of the round table and plough the solids off the outer circumference. From the table. the solids then fall into a conical chamber where they are picked up and carried into a transport line by nitrogen carrier gas. The overall range of

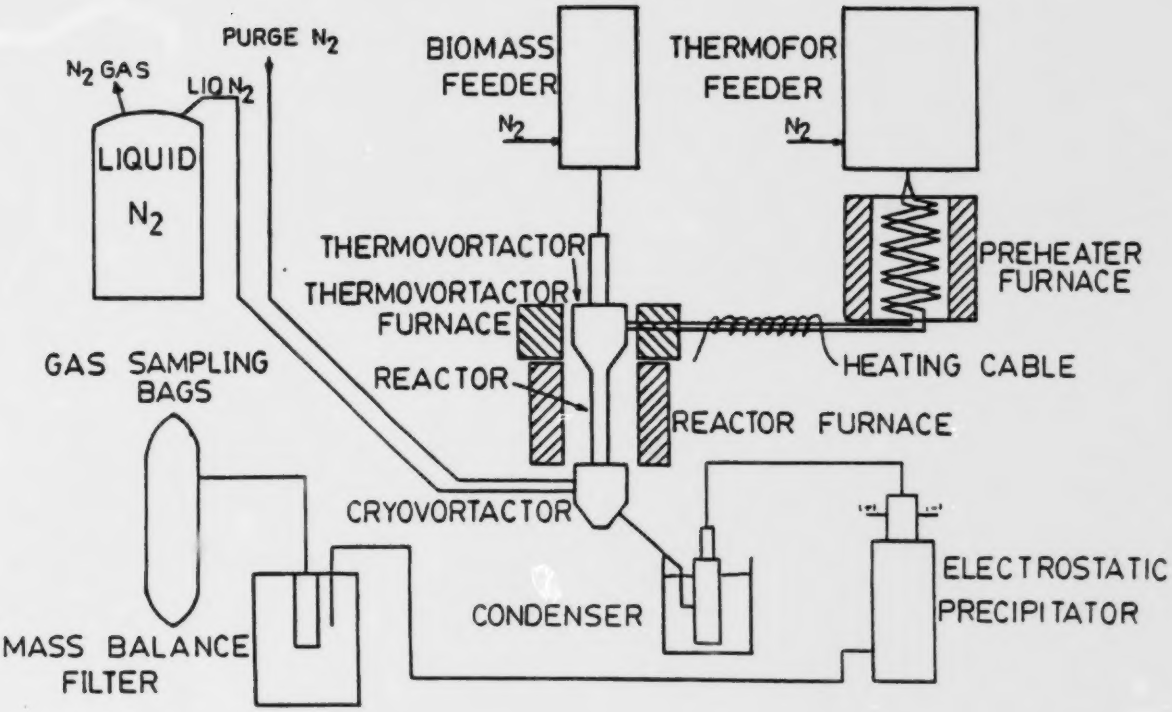


Figure 10. Current Ultrapyrolysis Flow Scheme

the feed rate of the solids is controlled by setting the gap between the lower funnel and the table. Fine control is exercised by the rotation speed of the table. Currently the biomass feeder is set in the range of 0 to 20 grams per minute and the thermofor feeder is set to deliver 0 to 200 grams per minute. The biomass feeder is mounted on a 60 kg balance to facilitate the determination of the mass balance. When thermofor solids are required to supply the process heat (i.e. either in place of gaseous nitrogen thermofor or as a supplement), the thermofor feeder sends cold (room temperature particulate solids to a double preheater coil assembly where they are heated to the appropriate temperature. These solids are then sent on to the Thermovortactor. Thermofor nitrogen can be sent directly to the preheater coil.

The fast pyrolysis of biomass is initiated in the Thermovortactor and continues in a plug-flow entrained bed downflow reactor. The reactor is simply a one meter length of Inconel pipe in an electrical oven. The mixture of hot gases and biomass passes from the Thermovortactor through the reactor to the Cryovortactor. With the insertion of cylindrical inserts to reduce the reactor volume and by manipulating thermofor/biomass flowrates, the residence time (i.e. the time from the heating of the biomass to the exit from the reactor) can be set between 30 and 900 ms. Reactor temperatures can be set in the range of 650 to 1000°C.

After exiting from the Cryovortactor, the product stream passes through the product recovery train which consists of a water-cooled cyclonic condenser, an optional electrostatic precipitator, a porous metal filter cartridge and a bank of four gas collection/sampling bags. A detailed design of the individual Ultrapyrolysis system components (including dimensions and materials of construction) along with the flow scheme of the original system are given in a previous publication [1]. The detailed designs of the cyclonic condenser, and electrostatic precipitator are given in Appendix 14.2.

7.0 SYSTEM CALIBRATIONS

All of the system components involved in the measurement of system operating parameters (pressure, temperature and flow) and mass balance (volume) were calibrated by at least one independent method. The detailed results of these calibrations are beyond the scope of this report but have been included in the regular progress reports to the National Research Council during the course of the project. A general summary of the calibrations is given in the following paragraphs.

All of the Ultrapyrolysis Bourdon pressure gauges were calibrated with mercury manometers where:

$P = \rho gh$

P = pressure (Pa)
ρ = mercury density at test conditions (kg/m^3)
g = gravitational constant ($9.81\ m/s^2$)
h = height of mercury column (m)

The readings from the pressure gauges were correlated to the actual pressure (P) for a number of points over the scale range. A linear regression of the data gave an equation relating scale reading to actual pressure. For twelve (12) pressure gauges, the correlation coefficients ranged from 0.989 to 1.000.

Although the type K thermocouples (Brampton Thermoelectric, Inc.) are certified to be at least ± 0.15% over the 0 to 1300°C (273 to 1573 K) temperature range, it was decided to check the system thermocouples with reference temperatures of 0°C, room temperature and 100°C using a high precision certified NSB thermometer. In addition, relative agreement of the thermocouples was checked by inserting them in an aluminum block which was then placed in an electrical resistance oven set at approximately 400°C. The thermocouple readings were given by a high accuracy DORIC TRENDICATOR 412A Indicator. The results clearly illustrated that the manufacturer certified accuracy was exceeded.

The rotameter sets used in the UP system were calibrated with a sharp edged orifice meter (corner taps) and checked with a wet test meter (corrected for vapour saturation). The rotameters were calibrated with dry air by the manufacturer and this calibration agreed very well with orifice meter and wet test meter (WTM) results using dry air. However the "corrected" manufacturers' calibration using nitrogen did not agree well with the orifice meter and WTM results (even though the orifice and WTM gave similar results). A review of the literature indicated that the normal extrapolation of calibration curves from one gas to another (by molecular weight comparison) does not work well for "round float" orifice meters. In fact, our non-round float calibrations performed in the first phase of the work on rotameters not used in the current Ultrapyrolysis system, did exhibit good agreement between manufacturers' calibrations (with air) and empirical calibrations regardless of the calibration gas used. The results of the orifice and WTM calibrations using nitrogen were therefore combined and correlated to rotameter setting by linear regression analysis. Correlation coefficients ranged from 0.9985 to 0.9996. The resulting equations were then used in the computer programs which calculated the residence time and mass balance. The pressure regression equations were also used in these programs.

The reliability of the mass balance procedures depends largely on the ability to acccurately measure the mass of non-condensible gas produced. The mass of the condensible products such as organic liquids and char can be measured quite accurately by gravimetric methods as long as the recovery process is reliable. As outlined in Chapter 9.0 (Experimental Procedure), the gas mass is measured by evacuating the total product gas into a tank of known volume. The pressure change is recorded, the average molecular mass is calculated from the gas analysis and the results are inserted into the ideal gas law to calculate the total gas mass. It was decided to verify the accuracy of this procedure by determining the volume of the tank by a reliable physical method and by testing the procedure using a known mass of gas (the gas analysis is constantly calibrated with a standard gas and is therefore given no further consideration in this discussion).

The tank volume was measured by the most practical and direct physical method available. The mass of water required to fill the vessel was recorded and its density at test conditions was used to calculate the volume. Two tests conducted by different experimenters gave results of 434.8 ℓ and 435.2 ℓ. An average value of 435.0 ℓ was therefore used in the mass balance procedure. A second method of calibration using a wet test meter (with flow corrected to remove the saturation volume) coupled to the pressurized tank, gave a volume estimate of 437 ℓ.

The integrity of the mass balance procedure for gas mass determination was verified using two separate methods. The first method closely resembled an actual experimental run with the exception that the mass and composition of the "product" gas was known a priori. Using a small gas bottle of fixed volume (0.95 ℓ) and known pressure, a known amount of tracer gas was injected into the Ultrapyrolysis system along with an appropriate flow of nitrogen carrier gas to simulate the dilution occuring during actual experimental conditions. The tracer gas was a gas chromatograph calibration gas standard. Using normal operating analytical and experimental procedures, 2.56 g of gas was injected into the system and 2.57 g was accounted for in the analysis.

The second method of mass balance procedure verification was less complex and time consuming, and was therefore repeated periodically during the project. Pure nitrogen was simply directed to the calibrated rotameters, through the Ultrapyrolysis system and eventually to the gas collection bags. The gas was then evacuated to the gas tank where its mass was determined by normal procedures (ideal gas law and pressure change at a given temperature). This value was then compared with the corresponding value calculated from the rotameter readings. No significant deviations were observed.

8.0 CELLULOSE/WOOD FEEDSTOCKS AND SOLID HEAT CARRIER

8.1 Cellulose and Wood Feedstocks

Woody biomass materials consist primarily of varying proportions of the three major constituents - cellulose, lignin and hemicellulose. In the Ultrapyrolysis study, the vast majority of experiments were conducted using only one of the three major wood components, namely cellulose. Additional studies were conducted using poplar and red maple. All three of these feedstocks were also used in the Waterloo University flash pyrolysis process which was amenable for comparison. All feedstocks were dried to approximately 0.9% moisture content (wet basis) prior to fast pyrolysis.

Avicel PH-102 crystalline cellulose supplied by the FMC corporation (Philadelphia PA) was used as the representative cellulose feedstock in the Ultrapyrolysis research program. It is a free-flowing white powder with an average particle size of 100 µm, an "as received" moisture content of 4.0 percent by mass (wet basis), and an empirical formula of $CH_{1.73}O_{0.87}$. Among the biomass feedstocks tested during the course of this project, cellulose had the highest hydrogen/carbon and oxygen/carbon mole ratios. The ultimate (elemental) analysis on a mass basis is given in Table 1. Avicel has been recommended as a standard for use in cellulose pyrolysis studies by the American biomass community at the National Science Foundation Workshop on "Research Goals of the Scientific Community concerned with the Thermochemical Conversion of Biologically-Based Raw Materials".

TABLE 1. CELLULOSE AND WOOD FEEDSTOCK ANALYSIS

FEEDSTOCK	ELEMENTAL ANALYSIS (mass %, dry basis) C	H	O	N	S	Ash	"AS RECEIVED"+ MOISTURE (% wet basis)	EMPIRICAL FORMULA C	H	O	N
Cellulose (Avicel)	43.3	6.3	50.3	0.02	0.001	0.03	4.0	1.0	1.73	0.87	-
IEA Poplar	49.3	6.1	44.1	0.1	-	0.4	5.2	1.0	1.47	0.67	-
Red Maple	48.5	6.2	44.2	0.5	-	0.6	7.0	1.0	1.52	0.68	0.01

+ All feedstocks were sized to 100 um and dried to 0.9 % moisture (wet basis) prior to pyrolysis

TABLE 2. THERMOFOR (SILICA/SAND) CHARACTERIZATION

U.S. SIEVE NO.	MILLIMETER DESIGNATION	MEAN % ON SIEVE	STANDARD DEVIATION	MEAN % CUMULATIVE	MEAN % PASSING
40	0.420	-	-	-	100.0
50	0.297	0.4	1.2	0.4	99.6
70	0.210	2.0	1.2	2.4	97.6
100	0.149	8.0	3.1	10.4	89.6
140	0.105	35.5	5.3	45.9	54.1
200	0.074	31.0	3.4	76.9	23.1
270	0.053	12.4	2.5	88.3	11.7
PAN	-	10.5	1.9	98.8	0.0

CHEMICAL ANALYSIS

SiO_2	99.188
Fe_2O_3	0.102
TiO_2	0.169
Al_2O_3	0.431
CaO	<.01
MgO	<.01
LOI *	0.10

* LOI - loss on ignition

Red maple and "standard" IEA (International Energy Agency) poplar supplied by Waterloo University (Dr. D.S. Scott) were used as the wood feedstocks. Both were dried, ground and sieved to give an average moisture content and particle size of 0.9% (wet basis) and 100μm, respectively. The standard IEA poplar has an empirical formula of $CH_{1.47}O_{0.67}$, and is well characterized in terms of elemental analysis (Table 1), higher heating value (19.5 MJ/Kg), age (7 years), clone (D38 populus deltoides) and lignocellulosic composition. This latter composition has been reported on a moisture-free mass basis as 53.4% cellulose, 23.4% lignin, 19.8% hemicellulose, 3% extractives and 0.5% ash. The ash received moisture content was 5.2% (wet basis).

Only the elemental analysis (Table 1) and the ash received moisture (7.0%, wet basis) were reported for the red maple. From the elemental analysis, the empirical formula $CH_{1.52}O_{0.68}N_{0.01}$ was calculated. Theander [159] reports a typical lignocellulosic composition of 42.0% cellulose, 25.4% lignin, 29.4% hemicellulose and 3.2% extractives for red maple.

8.2 Solid Heat Carrier

Although the heat carrier (thermofor) was gaseous nitrogen for the large majority of experiments summarized later in this report, a series of trials using solid particulate thermofor was conducted as well. The solid thermofor was simply F-140 grade non-porous silica sand purchased from Wilkinson Foundary Supplies (Toronto, Ontario). The average particle size was 100μm and the moisture content was less than 0.5% by mass. Other physical properties are summarized in Table 2.

9.0 EXPERIMENTAL PROCEDURE

In preparation for an experiment, the system is purged with nitrogen. The furnaces are then turned on and allowed to reach their setpoint temperatures. When the desired temperatures are reached, cryogenic nitrogen is injected into the Cryovortactor. Thermofor (i.e. transported silica sand and/or inert nitrogen gas) is then introduced into the system and the cryogenic nitrogen flowrate is adjusted to ensure that the Cryovortactor temperature is less than 350°C. Gaseous nitrogen was used as the thermofor for all of the experiments reported in this paper. During the startup period, the stream exiting from the reactor system is vented to atmosphere. The biomass feeder is activated and its feedrate is verified by directing the flow to a collection device mounted on an electronic balance. A cellulose feedrate of 4 to 6 grams per minute was typical for the experiments reported in this paper.

Immediately prior to the actual steady state experimental run, the thermofor/cryofor stream (which is exiting from the Cryovortactor) is directed to the mass balance filter and recovery train. The biomass is then directed to the Thermovortactor and the actual fast pyrolysis experiment is thereby initiated. Products which are initially cooled to a temperature in the range of about 300 to 350°C in the Cryovortactor, are further cooled to room temperature in a water-cooled cyclonic condenser/heat exchanger. Solids and condensibles are deposited in the condenser and the filter, and the entire non-condensible product gas is collected in the gas collection bags. For extremely short residence time trials (when the yield of "condensibles" increases), an electrostatic precipitator unit can easily be integrated in the downstream gas line. The steady state experiment continues for 5 to 20 minutes. At the end of the experiment, the biomass flow is redirected from the reactor system to the bypass line and its feeder motor is turned off. The inert thermofor and cryofor streams, however, are maintained for a short period of time in order to ensure that all products are carried to the recovery system. After purging, the recovery train (including filter, transport lines and condenser) is dismantled and washed with methanol to collect any condensibles. When sufficient quantities are produced, pure condensibles are poured from the condensor prior to solvent extraction. Recovery of the methanol-extracted pyrolysis liquids is accomplished using a rotary evaporator. Gas samples are taken from the collection bags and analyzed using a Carle refinery gas chromatograph (Model 111-H/197A). When gas analysis of the bag contents is completed, the gas is drawn into an evacuated Superior 123 USWG Propane tank of known volume. The magnitude of the change in tank pressure and the gas analysis are used to determine the quantity of the product gas.

10.0 RESULTS/DISCUSSION

10.1 Overview

For the purposes of this report, the results of the Ultrapyrolysis experimental program have been summarized within six (6) general sections which represent natural divisions of the work. The large majority of the program involved the fast pyrolysis of Avicel cellulose using gaseous nitrogen as the thermofor. A sufficient number of experiments were conducted to do an adequate statistical analysis of the kinetics which characterize the production of principal gases from cellulose. The wood pyrolysis experiments were carried out using IEA standard poplar and red maple, and give a good indication of the yields of gases, liquids and char which can be expected during fast pyrolysis. The number of experiments was not sufficient, however, to do a meaningful statistical analysis of the kinetic parameters. Cellulose and maple Ultrapyrolysis data were compared with the cellulose and maple flash pyrolysis data from the Waterloo University (Dr. D.S. Scott) fluidized bed process. The intention of this comparison was to check compatibility of the results and to summarize the trends of the products yields (of rapid pyrolysis) over an extended temperature range. Hydrocarbon cracking studies using ethane and methane as feedstocks were carried out to better characterize the role of secondary cracking reactions. A qualitative study of the water-gas shift was also conducted to determine whether it plays a significant role in fast pyrolysis. Finally, a limited number of fast pyrolysis experiments were conducted using solid thermofor (particulate sand) to determine whether any significant difference is evident. If not, then the results from experiments using gaseous nitrogen thermofor (which are much easier to conduct) can be used to predict results with sand thermofor.

The residence times are calculated using the reactor system volume (as a function of temperature to account for thermal expansion) and the mean volumetric flow rate. Since the large bulk of the volume is due to inert nitrogen carrier gas (~90%), it is reasonable to assume a constant volumetric flow rate. In the residence time model, however, linear decomposition kinetics of a characteristic primary tar (MW = 100) at the reactor inlet to the final product gas composition (MW = 24) at the reactor outlet, were assumed. This crude refinement gives a slightly better estimate of the average molecular weight of the gaseous stream within the reactor (which is used to calculate volumetric flowrate) than the assumption that the stream has an average molecular weight equal to that of its nitrogen carrier gas.

Due to the significant increase in the "turn around" time for an experiment, a complete mass balance (i.e. where liquids were solvent-extracted and recovered by rotary evaporation) was not carried out for all of the cellulose and wood pyrolysis trials. Complete mass balances are reported for about 30% of the cellulose experiments and about 70% of the wood experiments. A limited number of elemental balances (C,H and O) were carried out on cellulose fast pyrolysis trials after the liquids were analyzed by B.C. Research.

10.2 Fast Pyrolysis of Cellulose

A sample data sheet, sample printouts from the residence time and mass balance computer programs, and a product recovery data sheet are given for a typical Avicel cellulose pyrolysis experiment in Appendix 14.3. The "mass balance" as reported on the computer printouts is not complete; it accounts only for the gas product (i.e. no liquids), and is therefore consistently and significantly under 100 percent. The true mass balance (Table 11) is calculated by combining the results of the computer mass balance (i.e. for gases) to the liquid yields determined by rotary evaporation of the solvent-extracted products.

The results of the production of total gas and the individual gaseous components produced during the fast pyrolysis of Avicel cellulose at temperatures between 650 and 900°C, are given in Tables 3 to 10. The yields of total gas and liquid are plotted as a function of residence time in Figures 11 to 18, and the plots of the individual gaseous component yields are included in Appendix 14.4. These solid lines on the curves which correspond to the gas yield data, represent the fit of the data to a first-order kinetic model (discussed later). This model has been derived from a non-linear regression analysis. The general shape of the total gas yield curves (Figures 11 to 18) indicates an initial rapid production rate followed by a tapering off to an asymptotic (i.e. constant maximum) yield, and is representative of all of the curves (Appendix 14.4) for the yields of the principal gas components (i.e. H_2, CO, CO_2, C_2H_4, CH_4 and C_2H_2). Minor components such as ethane, propylene and benzene/toluene do not always

TABLE 3. CELLULOSE PYROLYSIS EXPERIMENTS (650°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H2	CO	CO2	C2H4	C3H6	C2H2	CH4	C2H6	B/T *
366	513	23.8	0.4	17.6	2.4	1.2	0.6	0.0	0.7	0.0	0.8
367	332	21.1	0.1	15.9	2.3	1.1	0.6	0.0	0.6	0.0	0.7
368	257	13.9	0.0	10.1	2.0	0.7	0.4	0.0	0.3	0.0	0.5
369	196	14.1	0.0	10.4	1.8	0.7	0.4	0.0	0.4	0.0	0.4
370	147	12.8	0.0	9.3	1.8	0.6	0.4	0.0	0.3	0.0	0.3
371	109	11.9	0.0	8.1	1.9	0.7	0.4	0.0	0.3	0.0	0.5
372	828	26.8	0.3	20.0	2.5	1.3	0.7	0.0	0.9	0.2	0.8
373	504	23.3	0.3	17.5	2.1	1.2	0.7	0.0	0.7	0.0	0.7
374	294	17.0	0.2	12.1	1.9	1.0	0.5	0.0	0.5	0.0	0.6
375	246	16.9	0.0	12.6	1.8	0.9	0.4	0.0	0.5	0.0	0.6
376	146	14.0	0.0	10.3	1.9	0.6	0.3	0.0	0.3	0.0	0.5
377	788	27.0	0.3	20.2	2.5	1.3	0.8	0.0	1.0	0.2	0.6

TABLE 4. CELLULOSE PYROLYSIS EXPERIMENTS (700°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H2	CO	CO2	C2H4	C3H6	C2H2	CH4	C2H6	B/T *
230	783	53.9	0.9	39.8	3.7	3.8	1.1	0.6	2.9	0.4	0.8
233	867	54.6	0.9	39.9	4.2	3.8	1.1	0.4	2.9	0.5	0.8
259	73	19.7	0.1	15.2	2.3	1.1	0.5	0.3	0.5	0.0	0.0
260	122	27.4	0.2	21.3	2.7	1.7	0.7	0.3	0.8	0.0	0.0
261	185	30.6	0.3	23.3	3.0	1.8	0.8	0.4	1.1	0.0	0.0
262	320	36.9	0.4	28.3	2.8	2.5	0.9	0.3	1.6	0.0	0.0
266	142	26.3	0.2	19.3	2.4	1.5	0.7	0.3	0.8	0.1	0.8
267	74	21.2	0.1	15.8	2.1	1.1	0.5	0.3	0.6	0.0	0.6
268	229	32.5	0.4	24.1	2.5	1.9	0.9	0.3	1.3	0.2	0.9
269	203	32.3	0.4	23.7	3.2	1.9	0.8	0.3	1.1	0.2	0.7
324	668	56.1	0.9	41.1	4.0	3.3	1.4	0.2	2.8	0.4	0.9
389	594	47.1	0.9	35.3	3.7	2.6	1.2	0.1	2.1	0.3	0.9
390	364	38.1	0.6	28.3	3.0	2.2	1.0	0.3	1.5	0.2	0.9
391	131	25.6	0.4	18.8	2.4	1.4	0.7	0.2	0.8	0.0	0.8
392	818	43.4	0.8	32.5	3.1	2.6	1.1	0.2	2.0	0.3	0.8
393	651	49.5	1.1	36.9	4.0	2.8	1.2	0.1	2.2	0.3	0.9
394	526	42.7	0.7	31.9	3.7	2.3	1.1	0.2	1.7	0.3	1.0

* B/T - benzene/toluene

TABLE 5. CELLULOSE PYROLYSIS EXPERIMENTS (750°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H2	CO	CO2	C2H4	C3H6	C2H2	CH4	C2H6	B/T*
231	456	68.1	1.2	49.6	4.8	5.4	1.0	0.9	3.9	0.5	0.8
234	806	71.2	1.4	51.9	4.9	5.6	1.0	0.6	4.7	0.5	0.8
236	575	70.5	1.3	51.2	4.9	5.4	1.1	0.8	4.3	0.4	1.0
237	177	49.2	0.7	35.9	4.0	3.5	1.0	0.7	2.1	0.3	0.9
270	103	40.0	0.5	29.4	3.4	2.5	1.0	0.5	1.6	0.2	0.8
271	74	34.5	0.4	25.5	3.0	2.2	0.9	0.4	1.1	0.3	0.9
272	216	60.3	1.0	44.4	3.7	4.2	1.3	0.8	3.4	0.4	1.1
273	304	64.6	1.1	47.4	4.0	4.6	1.2	0.8	4.0	0.5	1.0
283	287	62.2	1.2	45.4	5.1	4.1	1.2	0.5	3.5	0.4	0.9
284	66	40.4	0.6	29.8	3.3	2.7	1.0	0.6	1.3	0.4	1.0
311	717	74.4	1.3	54.1	5.4	5.4	1.4	0.6	4.7	0.6	1.0
325	606	64.9	1.2	47.6	4.6	4.4	1.2	0.4	4.1	0.5	0.9
395	692	68.8	1.3	50.8	4.7	4.5	1.5	0.4	4.0	0.6	0.9

TABLE 6. CELLULOSE PYROLYSIS EXPERIMENTS (800°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H2	CO	CO2	C2H4	C3H6	C2H2	CH4	C2H6	B/T*
263	124	61.4	0.9	45.4	4.5	5.2	1.0	0.9	3.3	0.1	0.0
264	69	52.8	0.7	39.7	3.8	4.3	1.0	1.0	2.3	0.0	0.0
265	203	69.6	1.3	50.6	4.9	5.4	1.1	0.8	4.3	0.5	0.8
274	100	62.3	1.1	45.5	4.0	4.9	1.2	1.0	3.2	0.4	0.9
275	202	79.1	1.6	57.1	5.4	6.3	1.2	1.1	5.0	0.5	0.9
276	178	75.7	1.5	54.5	5.3	6.0	1.1	1.0	4.8	0.5	0.9
288	218	73.7	1.4	52.9	5.4	5.5	1.2	1.0	4.7	0.6	1.0
289	73	51.2	0.8	37.6	3.3	3.6	1.2	0.8	2.3	0.3	1.2
290	112	55.9	0.9	40.7	4.0	3.9	1.1	0.9	2.8	0.4	1.1
308	290	83.6	1.5	60.2	5.9	6.2	1.3	1.2	5.4	0.7	1.2
309	463	81.7	1.6	58.8	5.9	6.0	1.1	1.0	5.8	0.5	0.9
312	230	71.8	1.3	51.5	5.4	5.7	1.2	1.0	4.2	0.5	1.1
378	390	79.1	1.7	57.4	5.3	6.1	1.1	0.8	5.3	0.5	1.1

* B/T - benzene/toluene

TABLE 7. CELLULOSE PYROLYSIS EXPERIMENTS (825°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T *
291	543	80.3	1.7	58.2	5.8	6.3	0.6	0.6	5.9	0.5	0.7
292	267	79.9	1.5	57.6	5.7	6.3	0.9	1.1	4.9	0.5	0.9
293	165	73.0	1.3	52.6	5.2	5.7	1.0	1.1	4.2	0.5	1.2
294	109	68.5	1.2	49.8	4.9	5.3	1.2	1.0	3.5	0.5	1.0
295	65	57.2	0.9	41.5	4.1	4.5	1.1	1.0	2.5	0.5	1.1
296	550	82.5	1.7	59.4	5.4	6.6	0.7	0.9	6.2	0.5	0.9
297	216	81.0	1.4	58.5	5.8	6.6	1.0	1.3	4.6	0.6	0.8
298	94	64.0	1.0	46.6	4.4	5.1	1.1	1.1	3.2	0.5	1.1
313	244	77.4	1.4	55.4	5.5	6.3	1.0	1.3	5.2	0.6	1.0
317	246	80.9	1.5	57.7	5.8	6.7	1.0	1.5	4.9	0.6	0.8
379	383	82.4	1.9	59.4	5.5	6.7	0.9	1.0	5.7	0.6	0.8

TABLE 8. CELLULOSE PYROLYSIS EXPERIMENTS (850°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T *
277	280	82.0	1.6	58.7	5.5	6.9	0.7	1.4	5.8	0.5	0.9
278	199	80.8	1.6	57.9	5.4	6.4	0.8	1.5	5.7	0.6	1.0
279	94	73.4	1.4	52.7	5.3	6.0	1.0	1.4	3.9	0.7	0.9
310	376	83.6	1.6	59.7	5.8	7.0	0.7	1.5	5.9	0.6	1.0
314	65	62.3	1.1	44.7	4.5	5.1	1.0	1.4	2.8	0.7	1.0
318	328	83.6	1.6	59.7	6.0	7.0	0.7	1.6	5.7	0.6	0.8
319	233	83.5	1.6	59.8	5.8	7.0	0.8	1.3	5.7	0.6	1.0
320	130	81.2	1.5	58.0	5.8	6.6	1.1	1.5	4.8	0.7	1.0
321	106	73.1	1.3	52.6	5.1	5.9	1.1	1.4	3.9	0.7	1.0
380	763	84.1	1.8	60.6	5.5	7.0	0.4	1.1	6.5	0.4	0.7

* B/T - benzene/toluene

TABLE 9. CELLULOSE PYROLYSIS EXPERIMENTS (875°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
299	184	84.5	1.6	60.2	5.7	7.1	0.6	1.9	5.5	0.6	1.3
300	263	86.3	1.7	61.9	5.7	7.2	0.6	1.8	6.0	0.6	0.9
301	157	85.5	1.7	61.5	5.9	6.9	0.7	1.6	5.5	0.6	0.9
302	96	84.5	1.7	60.4	5.8	6.8	0.8	1.8	4.6	0.8	1.1
303	96	76.3	1.4	54.4	5.7	6.4	0.8	1.8	4.2	0.8	0.8
304	78	78.5	1.3	55.9	5.9	6.7	1.1	2.0	4.0	0.7	0.8
305	156	77.7	1.5	55.4	5.4	6.5	0.8	1.5	5.1	0.6	0.9
306	228	87.2	1.7	62.2	5.7	7.4	0.4	1.6	6.7	0.5	1.0
307	485	87.9	1.7	62.8	5.7	7.5	0.4	1.6	6.7	0.5	1.0
387	363	87.2	1.9	62.4	5.7	7.4	0.5	1.5	6.4	0.5	0.9
398	57	74.5	0.8	53.9	5.5	6.1	1.1	1.5	4.1	0.6	0.9
399	57	74.4	0.7	54.0	5.1	6.1	1.2	1.5	4.1	0.6	1.0

TABLE 10. CELLULOSE PYROLYSIS EXPERIMENTS (900°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
253	234	87.9	1.7	62.4	6.3	7.4	0.5	1.8	6.1	0.6	1.2
254	164	87.1	1.6	62.0	6.1	6.8	0.4	2.3	6.2	0.5	1.3
280	255	86.2	1.7	61.4	5.9	7.7	0.4	1.9	5.9	0.5	0.8
281	182	85.6	1.8	60.8	6.1	7.3	0.6	1.8	5.9	0.6	0.9
282	105	85.1	1.7	60.7	5.8	7.3	0.8	1.8	5.3	0.7	0.9
381	678	92.8	2.2	66.8	5.9	7.6	0.2	1.6	7.2	0.3	1.0
382	104	82.7	1.6	59.4	5.7	6.9	0.7	1.9	5.1	0.7	0.8
383	435	90.8	1.9	64.8	6.0	7.7	0.3	2.0	6.8	0.4	1.0
384	592	86.1	1.9	61.9	5.5	7.1	0.2	1.7	6.6	0.3	1.0
385	93	86.1	2.0	61.4	5.8	7.1	0.8	1.8	5.3	0.7	1.0
386	408	89.3	1.9	63.6	6.5	7.3	0.3	1.8	6.5	0.4	1.0
396	56	80.9	0.7	58.3	5.8	6.6	1.1	1.7	4.6	0.7	0.9
397	56	79.3	0.8	57.1	5.8	6.6	1.1	1.7	4.5	0.7	1.0

* B/T - benzene/toluene

exhibit this behaviour since they appear to be cracking as they are also appearing at elevated temperatures. The initial production rates of the principal gases vary both with temperature and gas component. It is obvious that the asymptotic total gas yield increases from 28 percent (by mass) to 88 percent as the temperature is increased from 650°C to 900°C. Over this same temperature range, the maximum mass yields of hydrogen, carbon monoxide and carbon dioxide increase from 0.3 to 1.9, 21 to 63, and 2.3 to 6.0 percent, respectively corresponding values for ethylene (a valuable petrochemical feedstock), total unsaturates (i.e. olefins and alkynes) and total hydrocarbons are 1.3 to 7.3, 2.1 to 10.3, and 3.3 to 17.5 percent, respectively. These asymptotic values are taken from the results of the regression analysis and not from the data tables.

The total liquid yields (product water plus organics) as a function of temperature are also represented by solid lines in Figures 11 to 18. Since the char yields from cellulose are negligible, over the entire temperature range studied, the liquid yield curves are simply the inverse of the gas yield curves (i.e. 100 percent minus the gas yields). This technique is justified by the results of the mass balance. Liquid yields decrease to an asymptotic minimum value as a function of residence time for each temperature. The asymptotic values decrease from 72 to 12 percent by mass as temperature is increased from 650 to 900 °C. It is apparent from the curves that total liquid yields can be increased at each temperature by reducing the residence time. The maximum liquid yield observed during the course of the experiments was 88.1 percent (by mass) at 650°C and 109 ms.

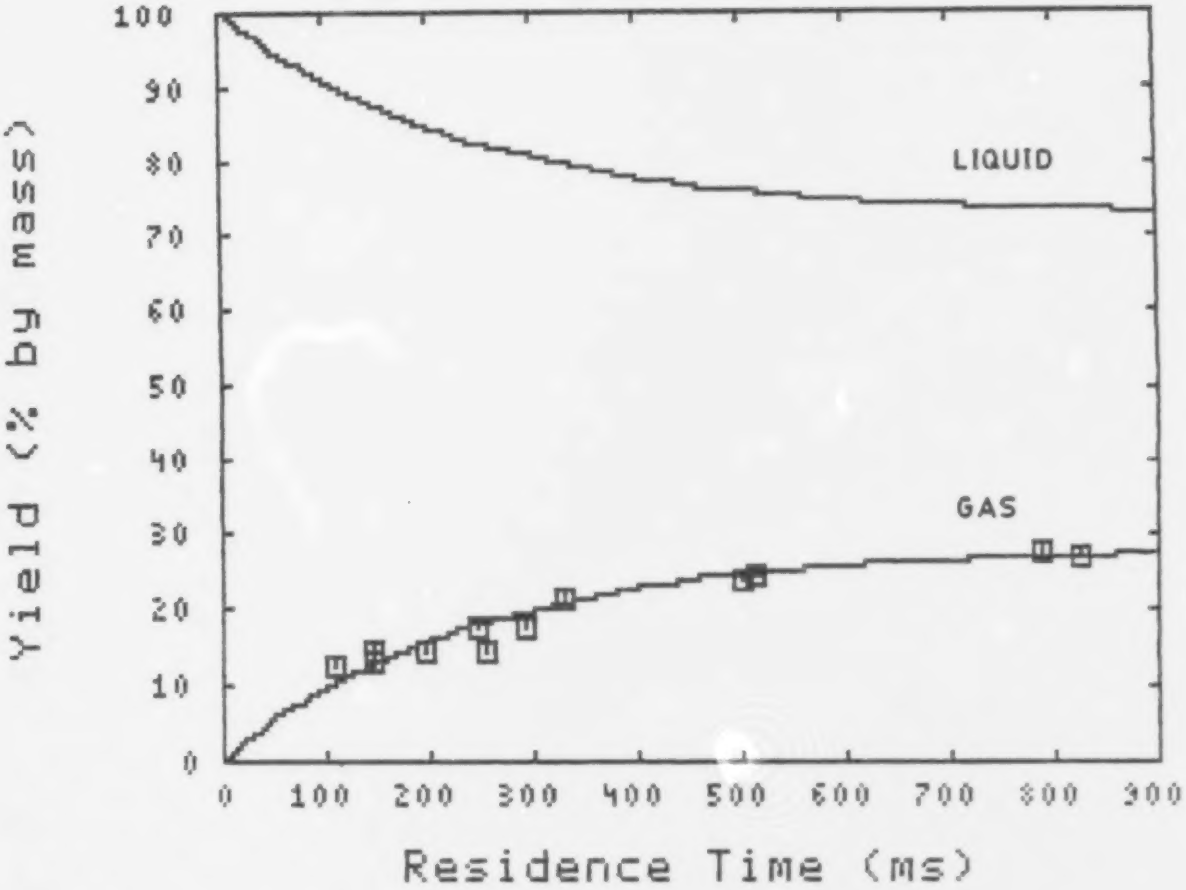


Figure 11. Fast Pyrolysis of Cellulose (650°C): Total Gas and Liquid Yields vs Residence Time.

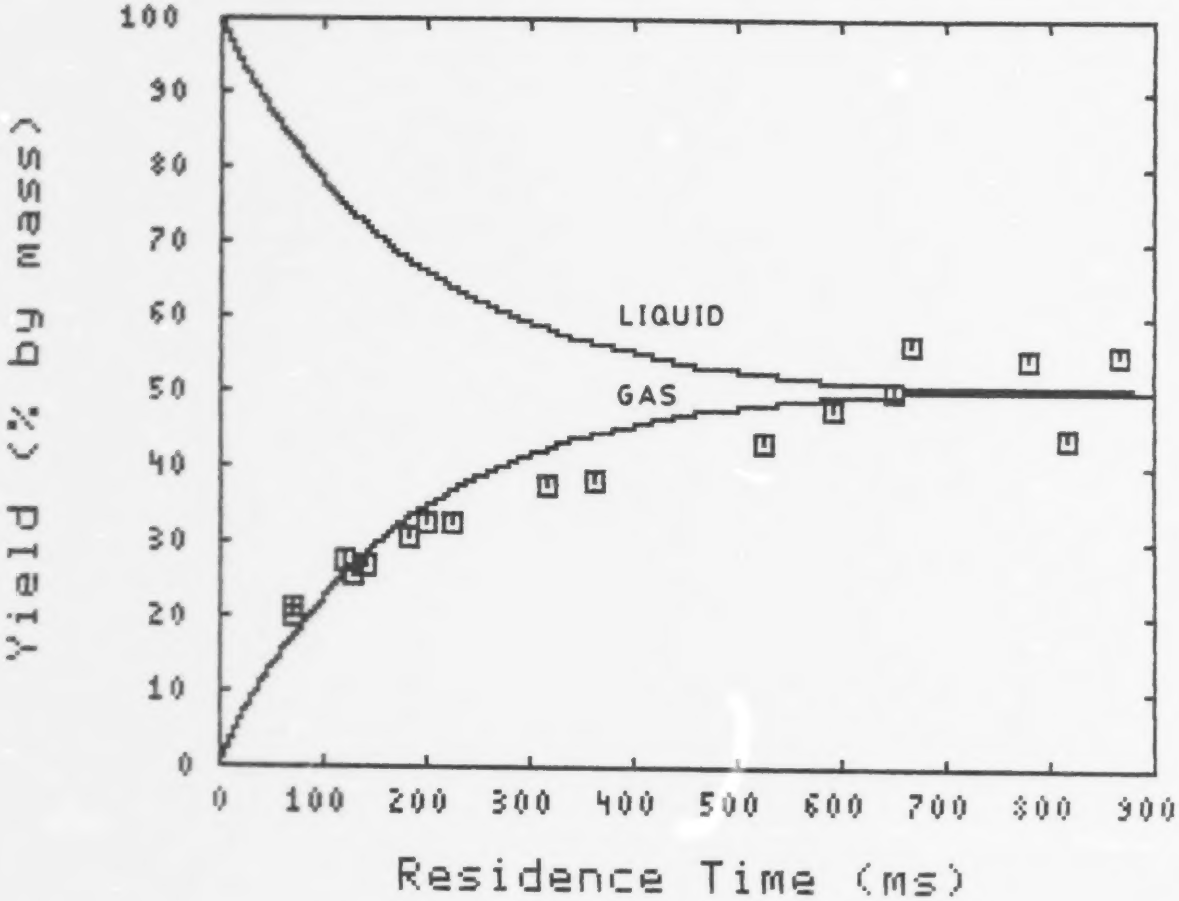


Figure 12. Fast Pyrolysis of Cellulose (700°C): Total Gas and Liquid Yields vs Residence Time.

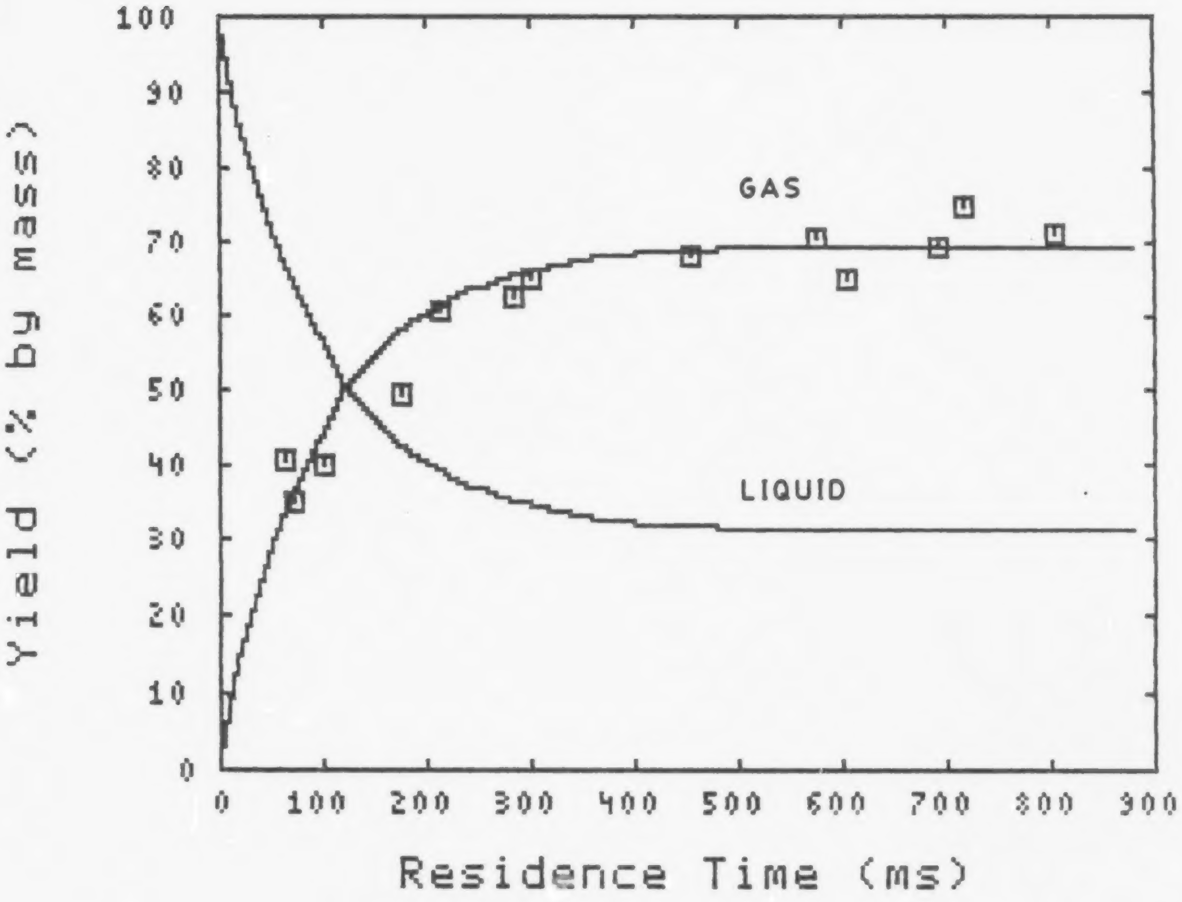


Figure 13. Fast Pyrolysis of Cellulose (750°C): Total Gas and Liquid Yields vs Residence Time.

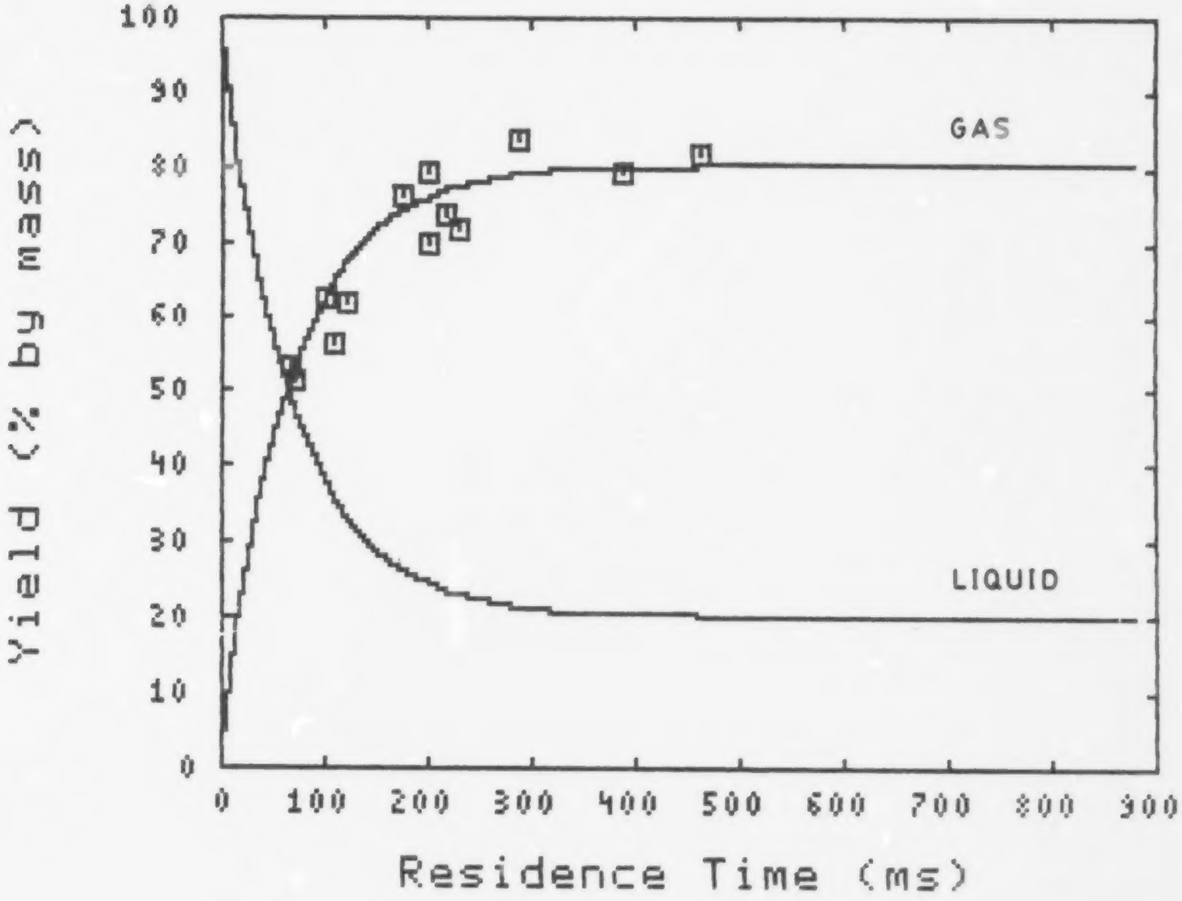


Figure 14. Fast Pyrolysis of Cellulose (800°C): Total Gas and Liquid Yields vs Residence Time.

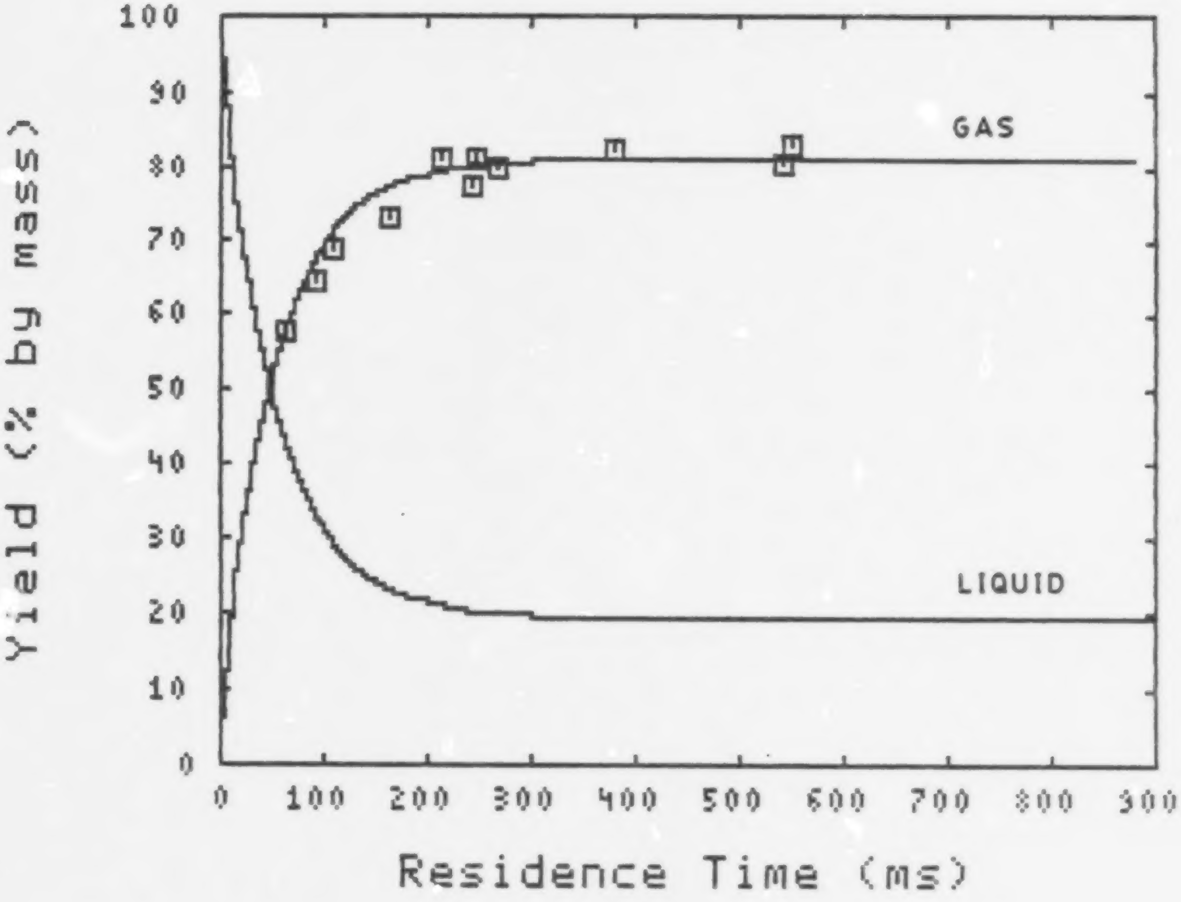


Figure 15. Fast Pyrolysis of Cellulose (825°C): Total Gas and Liquid Yields vs Residence Time.

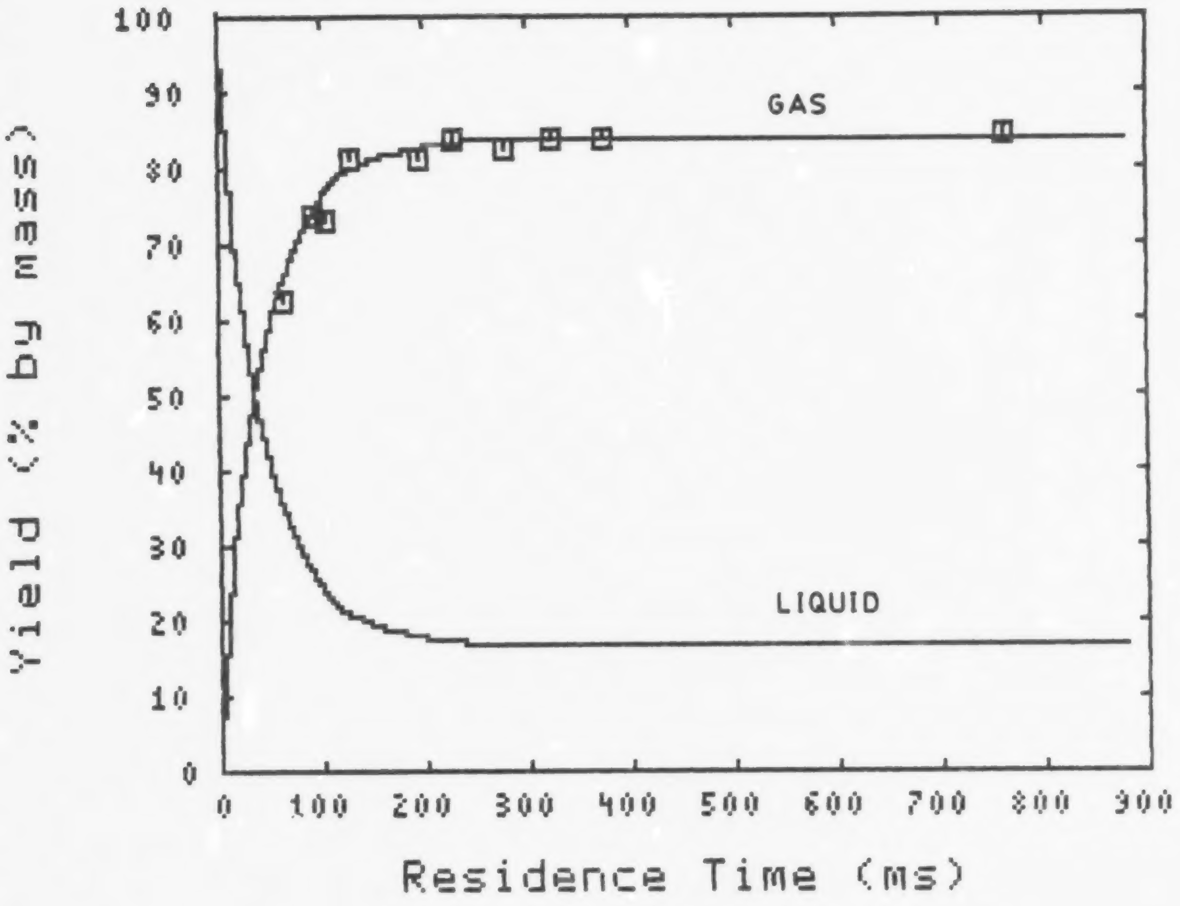


Figure 16. Fast Pyrolysis of Cellulose (850°C): Total Gas and Liquid Yields vs Residence Time.

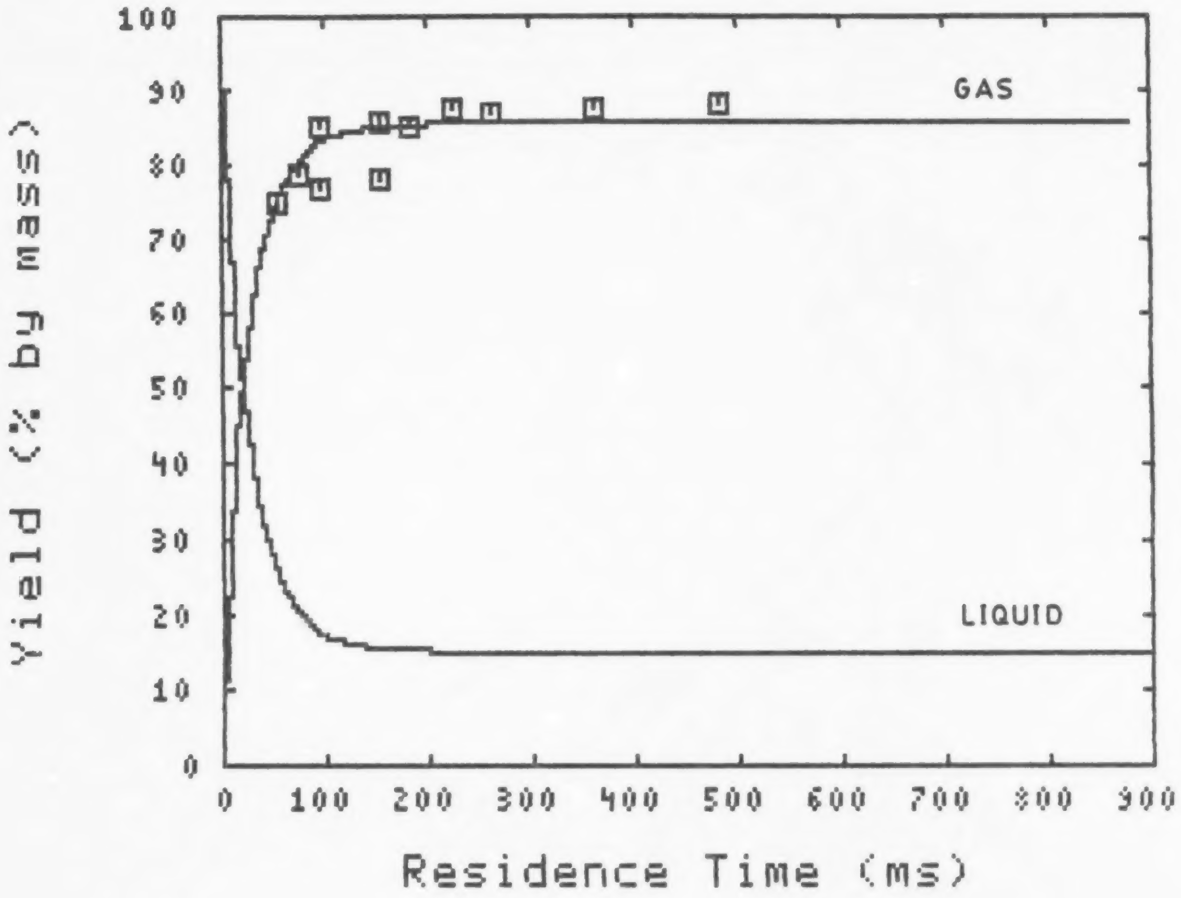


Figure 17. Fast Pyrolysis of Cellulose (875°C): Total Gas and Liquid Yields vs Residence Time.

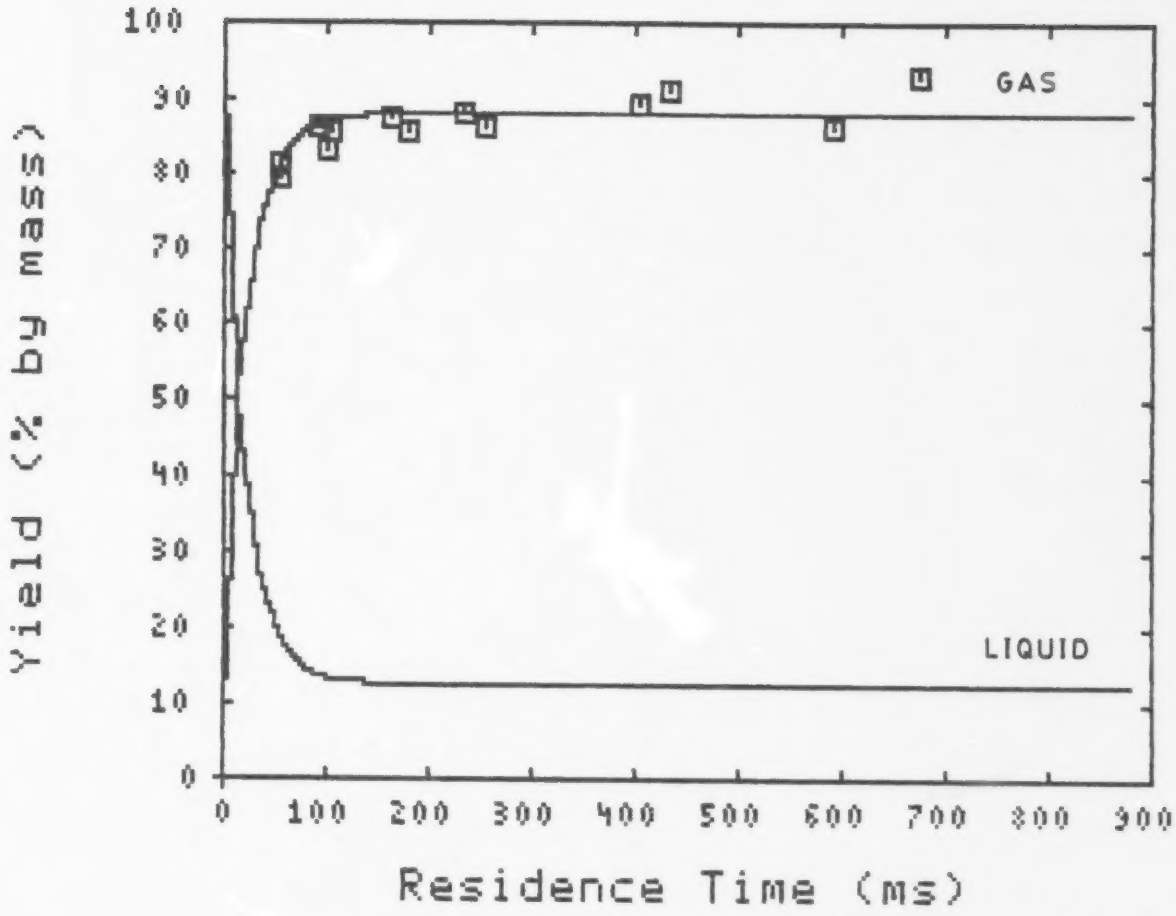


Figure 18. Fast Pyrolysis of Cellulose (900°C): Total Gas and Liquid Yields vs Residence Time.

A summary of the mass balance results for selected cellulose pyrolysis experiments is given in Table 11. The average value of the product recovery is 96.1 percent of the mass of cellulose pyrolyzed. This consistent deficit in the mass balance can be easily accounted for as the uncondensed water vapour in the saturated nitrogen carrier gas which exits from the condenser at 10°C. In addition, the small amount of light organic volatiles which are condensed but then lost with the solvent during rotary evaporation, can not be accounted for in the mass balance. However, the large portion of the light volatiles remains in the nitrogen carrier gas and is analyzed as a single peak on the Carle gas chromatograph. The product recovery ranged from 91.3 to 104.3 percent by mass. This latter value was the only value over 100 percent.

A summary of the elemental balance results for several selected cellulose pyrolysis experiments is given in Table 12. The elemental analysis of the liquids was carried out by B.C. Research (Vancouver) while that of the gases was provided by appropriate calculations using the gas chromatograph results. The elemental composition of the char component was taken from typical values in the literature. Any errors associated with this assumption for char will be negligible since the mass yield of char from cellulose pyrolysis is practically negligible. The carbon balance ranged from 94 to 101 percent (output/input) with a mean of 98%. Hydrogen and oxygen balances ranged from 100 to 127 and 97 to 103 percent, respectively, with mean values of 108 and 99 percent, respectively. Although the elemental balance is quite remarkable considering that five samples were randomly selected and

TABLE 11. CELLULOSE PYROLYSIS MASS BALANCE SUMMARY

RUN NUMBER	CELLULOSE FED (g)	PRODUCT RECOVERY (g)				TOTAL RECOVERY (% by mass)
		GAS	LIQUID *	CHAR	TOTAL	
CK300	35.6	30.45	3.86	0.06	34.4	96.6
CK303	26.5	20.04	5.75	0.09	25.9	97.7
CK304	21.2	16.49	3.64	0.12	20.3	95.8
CK305	49.7	38.28	9.46	0.04	47.8	96.2
CK306	39.5	34.13	2.60	0.08	36.8	93.2
CK307	41.8	36.42	2.70	0.06	39.2	93.8
CK309	51.8	41.92	7.40	0.04	49.4	95.4
CK310	50.7	42.17	6.30	0.05	48.5	95.7
CK311	43.3	31.93	9.45	0.21	41.6	96.1
CK313	34.2	26.22	5.94	0.10	32.3	94.4
CK314	23.3	14.40	7.98	0.34	22.7	97.4
CK318	37.7	31.25	4.65	0.06	36.0	95.5
CK319	39.0	32.28	5.12	0.09	37.5	96.2
CK320	37.5	30.17	6.18	0.06	36.4	97.1
CK321	30.8	22.32	7.56	0.05	29.9	97.1
CK324	32.0	17.80	13.52	0.25	31.6	98.8
CK325	35.2	22.63	11.84	0.10	34.6	98.3
CK366	16.4	3.87	11.73	0.40	16.0	97.6
CK367	11.6	2.43	9.54	0.10	12.1	104.3
CK369	21.6	3.01	17.41	0.44	20.9	96.8
CK370	21.6	2.74	17.69	0.35	20.8	96.3
CK374	26.3	4.42	20.92	0.25	25.6	97.3
CK375	23.6	3.95	18.98	0.46	23.4	99.1
CK379	21.8	17.80	2.05	0.02	19.9	91.3
CK381	20.8	19.12	1.00	0.03	20.2	97.1
CK382	22.2	18.19	2.31	0.05	20.6	92.8
CK383	25.4	22.86	2.02	0.02	24.9	98.0
CK384	29.7	25.36	3.10	0	28.5	96.0
CK385	24.4	20.81	2.94	0.01	23.8	97.5
CK393	21.0	10.29	10.21	0.04	20.5	97.6
CK394	24.6	10.42	13.65	0.07	24.1	98.0

* "Liquid" includes liquids recovered by solvent extraction and light volatiles in product gas stream.

TABLE 12. CELLULOSE PYROLYSIS ELEMENTAL BALANCE SUMMARY

RUN NUMBER	ELEMENTAL MASS (g)						ELEMENTAL BALANCE (% Output/Input)		
	OUTPUT			INPUT					
	C	H	O	C	H	O	C	H	O
CK366	7.1	1.1	8.0	7.0	1.0	8.2	101	106	98
CK369	8.8	1.4	10.8	9.3	1.4	10.5	95	100	103
CK370	8.7	1.5	10.6	9.3	1.4	10.9	94	107	97
CK374	11.1	1.9	13.0	11.3	1.5	13.3	98	127	98
CK375	10.1	1.6	12.1	10.1	1.5	12.0	100	107	101
MEAN VALUES (ELEMENTAL BALANCE)							98	105*	99

* As discussed in text, this "adjusted" mean does not include the value of 127 %. The non-adjusted mean is 109 %.

products were analyzed at two independent laboratories (i.e. gases at U.W.O. and liquids at B.C. Research), the relatively high value of the hydrogen balance is largely due to a single sample (127%). If the results of this sample are discarded (assuming the analysis may be in error), then the "adjusted" mean for the hydrogen balance is 105 percent. Overall, the results of the elemental and mass balances support the accuracy of the individual product analyses and also give credence to the reported mass yields of the individual components. In turn, this supports the utility of the data for kinetic modeling.

10.3 Fast Pyrolysis of Wood

IEA (International Energy Agency) "standard" poplar and red maple were pyrolyzed during the course of the experimental program. The results of the production of total gas and the individual gaseous components produced during the fast pyrolysis of IEA poplar at temperatures between 700 and 850 °C, are given in Tables 13 to 17. The total gas liquid (incl. product water and organics), and char yields are plotted as a function of residence time in Figures 19 to 23. Corresponding curves for the individual gaseous components are included in Appendix 14.5. As was the case for the cellulose data, the solid lines on the curves which correspond to the gas yield data represent the results of the first-order kinetic model (discussed later). The general shape of the curves is also similar to the cellulose pyrolysis curves in that the total gas yield (and the yields of the principal gaseous components) is characterized by an initial rapid production rate followed by a tapering off to an asymptotic maximum yield.

TABLE 13. IEA POPLAR PYROLYSIS EXPERIMENTS (700°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%) Gas	H2	CO	CO2	C2H4	C3H6	C2H2	CH4	C2H6	* B/T
10	462	39.9	0.2	24.2	8.1	2.0	0.5	0.2	2.4	0.5	1.6
11	298	36.9	0.2	21.9	7.8	1.8	0.7	0.2	2.3	0.4	1.6
12	204	33.0	0.1	19.0	7.9	1.4	0.6	0.2	1.8	0.5	1.5
13	123	28.7	0.1	16.0	7.7	1.1	0.5	0.0	1.5	0.4	1.3
14	90	25.4	0.0	14.0	7.1	1.0	0.5	0.0	1.3	0.5	1.1
16	345	32.2	0.2	18.7	7.4	1.4	0.6	0.1	2.1	0.4	1.3
17	177	32.7	0.1	19.2	7.7	1.3	0.6	0.2	1.8	0.4	1.4
18	123	25.0	0.1	14.6	6.2	0.9	0.5	0.1	1.3	0.3	1.0
19	671	36.8	0.2	22.9	6.6	1.8	0.8	0.2	2.5	0.3	1.5
20	323	38.2	0.2	23.6	7.1	1.9	0.7	0.3	2.4	0.4	1.7
21	719	40.3	0.3	25.1	7.1	2.0	0.8	0.2	2.7	0.4	1.8
37	510	40.2	0.3	25.7	7.0	1.9	0.8	0.2	2.5	0.4	1.3

TABLE 14. IEA POPLAR PYROLYSIS EXPERIMENTS (750°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%) Gas	H2	CO	CO2	C2H4	C3H6	C2H2	CH4	C2H6	* B/T
39	496	59.6	0.6	37.1	9.3	3.4	1.1	0.5	4.6	0.6	2.4
41	339	54.7	0.6	34.2	8.7	3.0	1.0	0.4	3.9	0.6	2.3
42	166	43.8	0.4	27.5	7.4	2.2	0.8	0.3	2.8	0.4	1.8
43	114	41.8	0.4	26.4	6.9	2.1	0.8	0.3	2.7	0.4	1.8
44	595	58.7	0.7	36.3	9.4	3.3	1.1	0.4	4.5	0.5	2.5
45	205	45.9	0.4	27.3	9.0	2.4	0.8	0.3	3.0	0.5	2.1
46	356	59.3	0.6	34.2	11.9	3.2	1.1	0.4	4.6	0.6	2.8
47	251	54.5	0.5	31.5	11.0	2.9	1.0	0.4	4.1	0.8	2.4
48	151	44.7	0.4	26.2	9.5	2.2	0.8	0.3	2.9	0.5	2.0
49	199	46.5	0.4	27.1	9.5	2.3	0.9	0.2	3.1	0.7	2.2
50	133	47.2	0.4	27.3	9.8	2.3	0.9	0.3	3.0	0.9	2.4
74	65	37.0	0.1	22.7	7.8	1.7	0.7	0.3	1.9	0.5	1.5

* B/T - benzene/toluene

TABLE 15. IEA POPLAR PYROLYSIS EXPERIMENTS (800°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
22	527	69.1	0.9	41.9	10.8	4.3	1.0	0.6	5.6	0.6	3.3
24	236	60.3	0.6	37.1	9.4	3.5	0.9	0.6	4.5	0.7	3.1
25	141	52.3	0.6	31.9	9.2	2.7	0.9	0.4	3.2	0.6	2.6
26	92	48.5	0.5	29.4	8.6	3.1	0.8	0.5	2.8	0.7	2.2
29	71	42.8	0.4	26.0	7.9	2.2	0.7	0.4	2.5	0.7	1.9
30	474	65.3	0.9	40.2	9.6	4.3	0.9	0.7	5.5	0.6	2.8
31	273	66.5	0.8	41.0	9.9	4.3	1.0	0.7	5.0	0.7	3.0
32	345	65.3	0.8	39.9	10.1	4.2	0.9	0.7	5.4	0.6	2.7
33	623	69.6	1.1	42.0	10.6	4.7	0.9	0.8	5.9	0.6	2.9
34	195	65.1	0.8	40.0	10.0	3.9	1.0	0.7	5.0	0.6	3.0
35	128	55.9	0.6	34.8	8.6	3.3	1.0	0.5	3.9	0.7	2.5
36	107	51.8	0.6	32.5	7.9	3.0	0.9	0.5	3.7	0.5	2.2
38	76	53.3	0.6	33.8	7.8	3.2	0.9	0.6	3.2	0.8	2.6
75	61	52.2	0.2	30.6	7.1	3.1	1.0	0.5	3.4	0.9	2.4
83	62	45.1	0.2	29.7	5.1	2.6	0.8	0.4	3.1	0.9	2.3

TABLE 16. IEA POPLAR PYROLYSIS EXPERIMENTS (825°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
62	334	70.5	0.9	41.5	11.5	4.6	0.9	0.8	6.0	0.7	3.6
63	282	74.7	0.9	44.2	12.7	4.8	1.1	0.8	6.4	0.8	3.1
64	233	70.9	0.9	41.5	12.4	4.5	1.1	0.7	5.9	0.8	3.2
65	139	63.6	0.8	37.5	11.1	3.9	1.0	0.6	4.9	0.7	3.0
66	580	72.8	1.0	42.5	12.1	4.8	1.0	0.7	6.5	0.6	3.7
67	117	69.8	0.8	40.4	12.8	4.0	1.2	0.7	5.3	0.9	3.6
68	442	74.6	1.0	44.0	12.2	4.9	1.0	0.8	6.5	0.7	3.5
69	530	74.9	0.9	44.3	12.5	4.9	1.0	0.7	6.6	0.6	3.4
70	177	71.2	0.7	40.9	13.1	4.2	1.2	0.7	5.6	0.8	4.0
71	154	64.4	0.7	37.5	11.7	4.0	1.0	0.6	5.2	0.7	3.0
72	185	71.6	0.8	42.4	12.8	4.2	1.2	0.7	5.7	0.8	3.1
80	61	49.3	0.2	29.6	9.1	2.8	0.8	0.4	3.2	1.1	2.1
82	61	51.4	0.3	31.2	9.0	2.8	0.9	0.5	3.6	0.8	2.4

* B/T - benzene/toluene

TABLE 17. IEA POPLAR PYROLYSIS EXPERIMENTS (850°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
51	321	72.0	1.0	42.5	12.1	4.8	0.9	0.9	6.1	1.0	2.7
52	398	74.4	1.2	43.8	12.2	5.1	0.7	1.0	6.7	0.6	3.1
55	588	76.7	1.2	46.2	12.0	5.3	0.7	1.0	6.9	0.6	3.0
56	121	75.9	0.9	43.0	11.9	4.6	1.0	0.8	5.9	1.0	3.8
57	108	67.4	0.8	39.8	11.2	4.3	1.0	0.8	5.2	0.9	3.4
58	582	71.4	1.3	42.8	11.2	4.9	0.7	0.9	6.5	0.6	2.7
59	85	70.0	0.8	41.8	11.8	4.2	0.9	0.9	4.8	0.9	4.1
60	368	74.2	1.1	44.5	11.8	5.1	0.9	0.9	6.5	0.6	2.8
61	97	69.0	0.8	40.4	12.1	4.2	1.1	0.7	5.5	0.9	3.4
73	87	64.7	0.7	38.4	11.1	4.0	1.0	0.8	4.8	0.9	3.2
77	248	72.0	0.5	44.1	11.3	4.9	0.9	0.9	6.3	0.8	2.4
78	270	74.5	0.8	44.5	11.5	4.9	0.9	0.9	6.3	0.7	4.0
79	62	65.1	0.4	38.6	11.3	4.0	1.1	0.8	4.3	1.2	3.5
81	325	71.2	0.8	42.8	11.5	4.7	0.9	0.7	6.3	0.6	2.9

* B/T - benzene/toluene

The asymptotic total gas yield increases from 39 percent to approximately 73 percent as the temperature is increased from 700 to 850 °C. Over this same temperature range the asymptotic yields of hydrogen, carbon monoxide and carbon dioxide increase from 0.3 to 1.0, 24 to 44 and 7.4 to 11.7 percent, respectively. Corresponding values for ethylene, total unsaturates and total hydrocarbons are 2.0 to 5.0, 3.0 to 7.0 and 6.1 to 14.5 percent, respectively. These asymptotic values are taken from the results of the regression analysis and not from the data tables.

The total liquid yields from poplar are also represented by solid lines in Figures 19 to 23. These curves are not simply the inverse of the gas yield curves, as was the case for the cellulose experiments, since the char yields are not negligible. The char yields were found to be independent of residence time for each temperature, and therefore the liquid yields are taken to be the difference between the total poplar feedstock mass and the mass of total gases plus char. The use of this approach to generate the liquid yields is justified by the results of the mass balance (Table 18).

As illustrated in Figures 19 to 23, the asymptotic values of the liquid yields (representing the minimum liquid yields at each temperature) decrease from 57 to 26 percent by mass as the temperature is increased from 700 to 850 °C. The total liquid yields could be drastically increased at each temperature simply by reducing the reactor residence time from the asymptotic region. The maximum

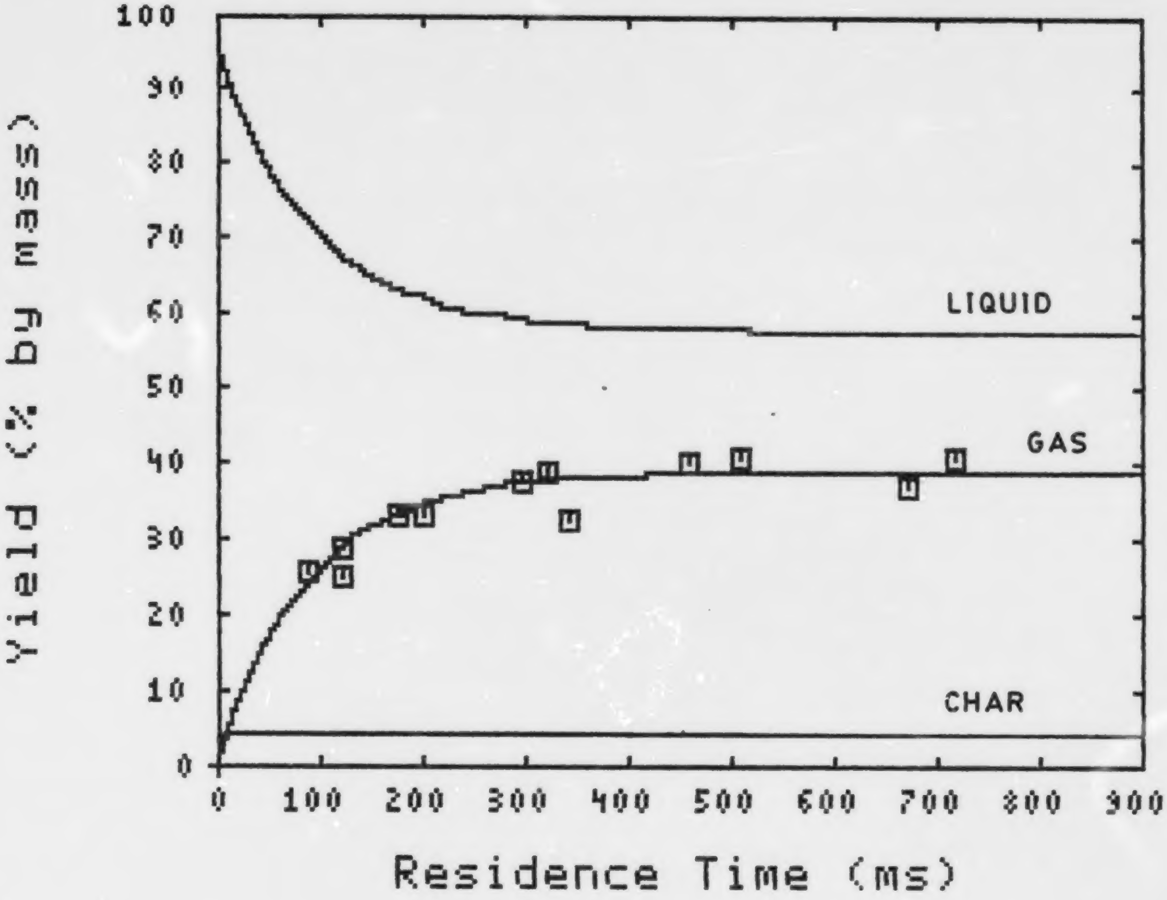


Figure 19. Fast Pyrolysis of Poplar (700°C): Total Gas, Liquid and Char Yields vs Residence Time.

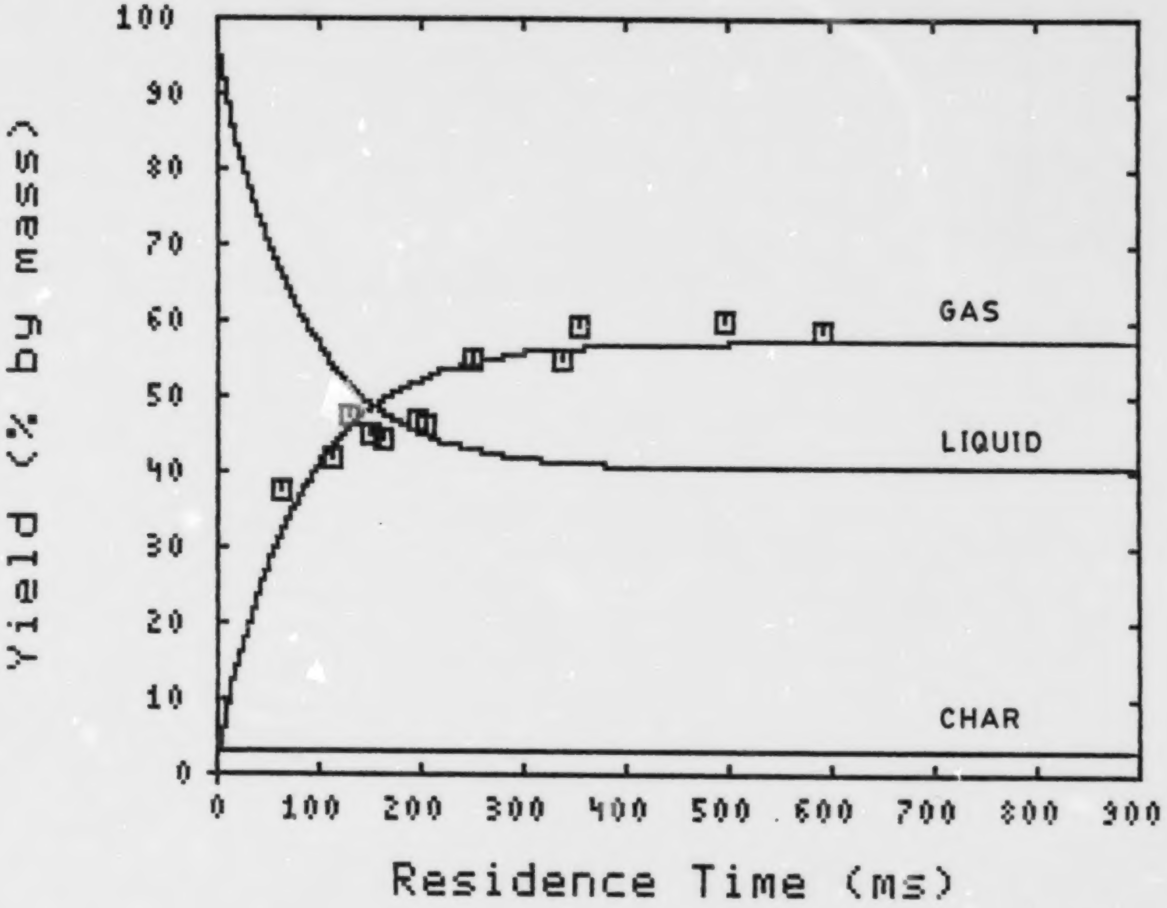


Figure 20. Fast Pyrolysis of Poplar (750°C): Total Gas, Liquid and Char Yields vs Residence Time.

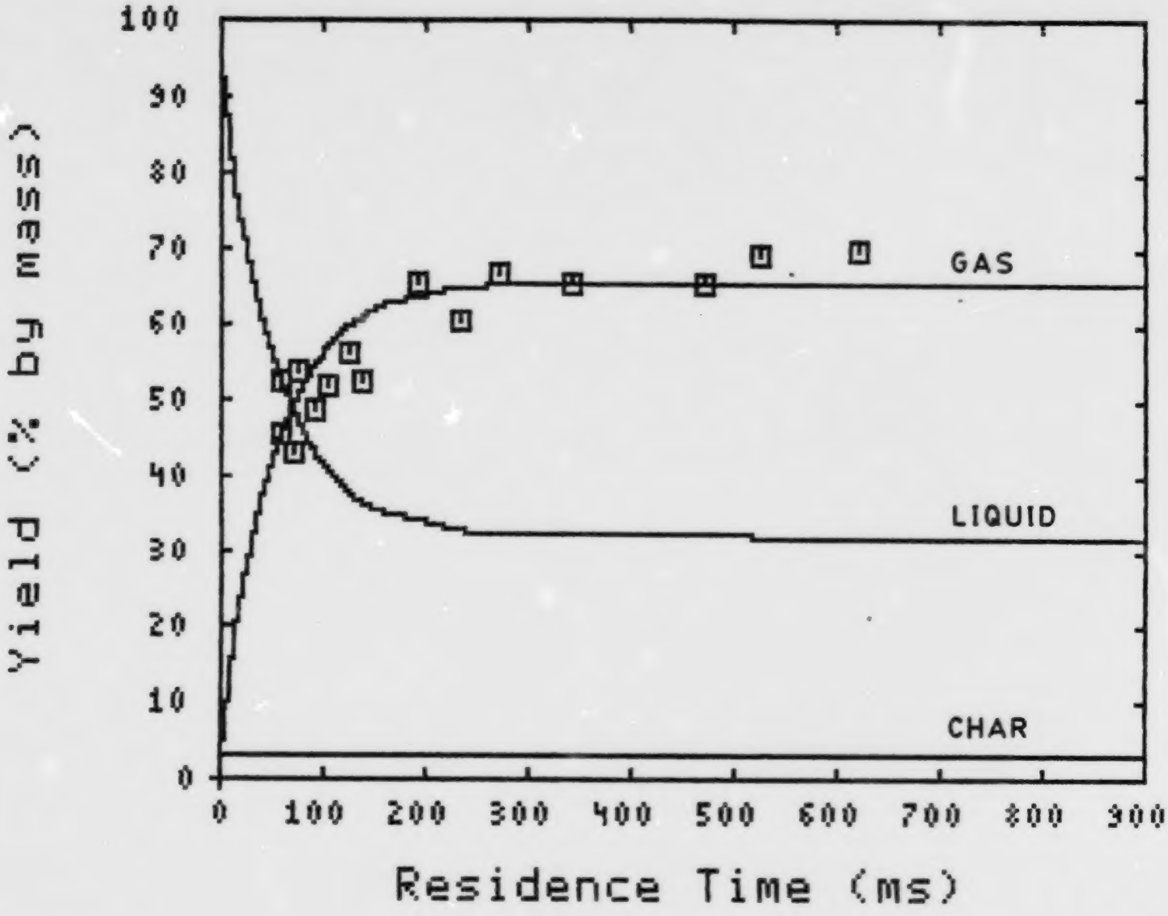


Figure 21. Fast Pyrolysis of Poplar (800°C): Total Gas, Liquid and Char Yields vs Residence Time.

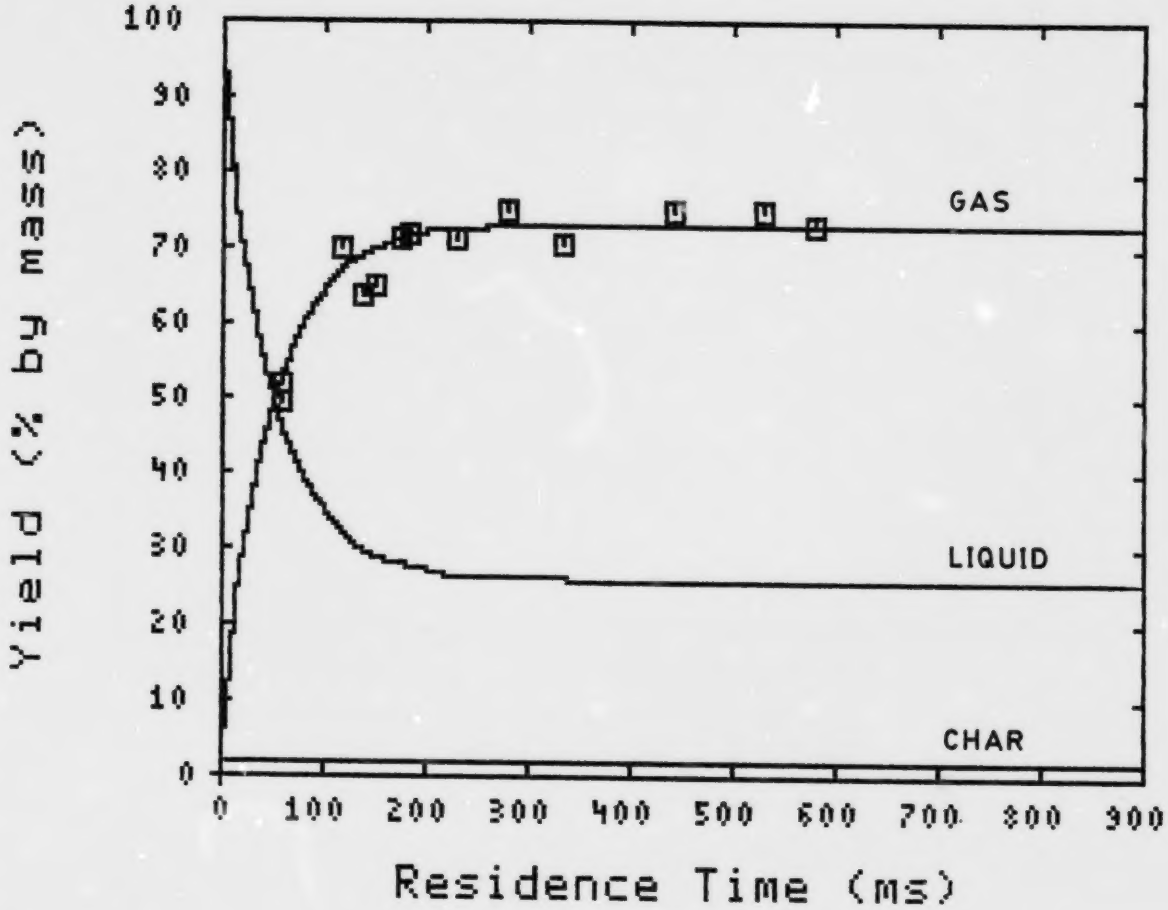


Figure 22. Fast Pyrolysis of Poplar (825°C): Total Gas, Liquid and Char Yields vs Residence Time.

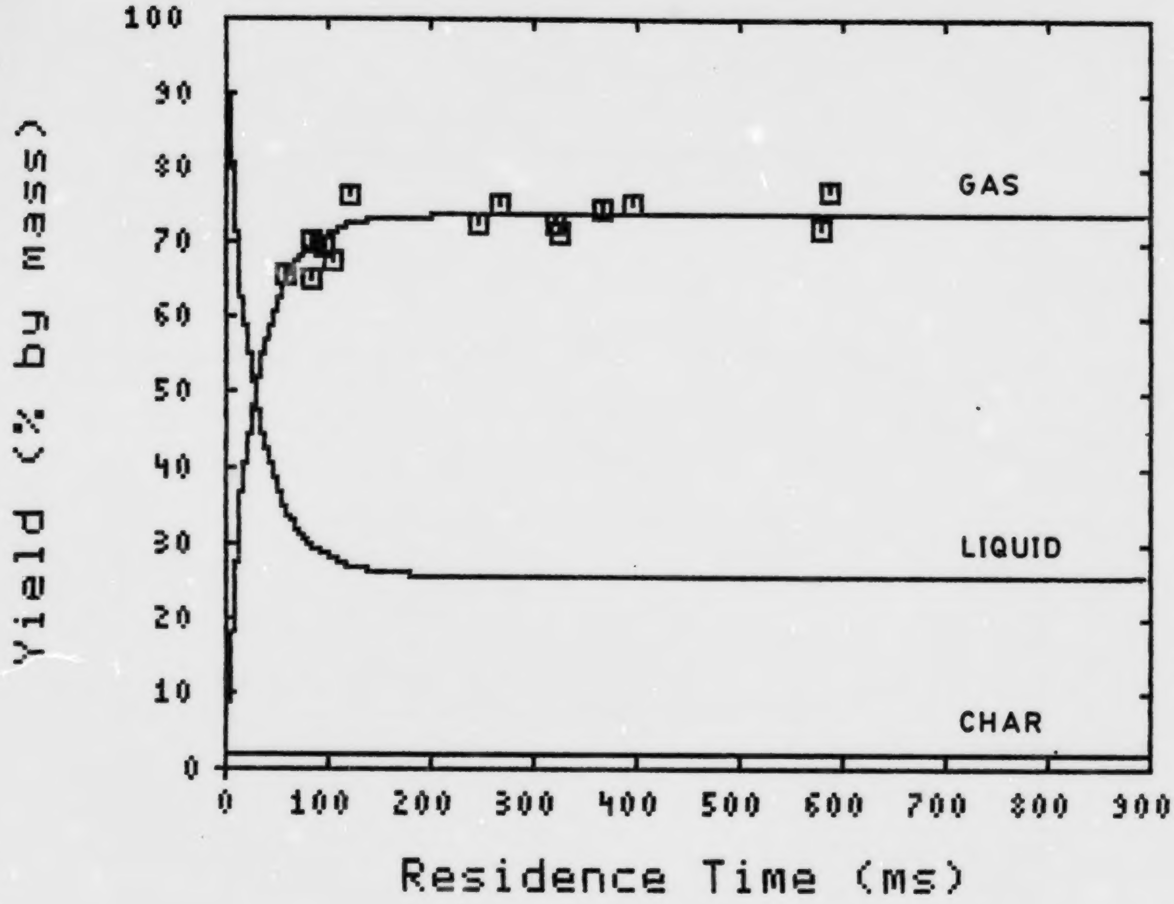


Figure 23. Fast Pyrolysis of Poplar (850°C): Total Gas, Liquid and Char Yields vs Residence Time.

liquid yields observed during the poplar experiments was approximately 70 percent at 700°C and 123 ms. No poplar experiments were conducted under 700°C where higher liquid yields are probable at the lower residence times.

Char yields were measured for 90 percent of the poplar experiments. It was apparent from the results that these yields were dependent upon reactor temperature but independent of the residence time. As illustrated in Figures 19 to 23, the char yields decrease from 4.1 to 1.3 percent of the poplar feedstock mass as the temperature is increased from 700 to 850 °C.

Mass balances were carried out on more than half of the poplar experiments, and a summary of the results is given in Table 18. The average value of the product recovery is 96.5 percent of the mass of poplar pyrolyzed. As was the case for cellulose experiments, the consistent deficit in the mass balance can easily be accounted for as uncondensed water vapour in the saturated carrier gas. The product recovery ranged from 92.9 to 105.6 percent by mass. Only two values (out of 36 mass balance experiments) were over 100 percent.

In order to allow a general comparison of the results of the poplar experiments with these of a second wood species, a limited number (i.e. less than thirty) of fast pyrolysis experiments were conducted using red maple. This feedstock was of a similar particle size (i.e. 100 μm) and moisture content (0.9% as fed) as the cellulose and poplar feedstocks. The results of the production of

TABLE 18. IEA POPLAR PYROLYSIS MASS BALANCE SUMMARY

RUN NUMBER	POPLAR FED (g)	PRODUCT RECOVERY (g)				TOTAL RECOVERY (% by mass)
		GAS	* LIQUID	CHAR	TOTAL	
PWK12	24.9	8.1	15.6	0.7	24.4	98.0
PWK14	25.8	6.5	17.8	1.1	25.4	98.5
PWK15	28.8	9.2	19.6	1.6	30.4	105.6
PWK17	23.9	7.8	14.2	1.2	23.2	97.1
PWK18	24.9	6.2	16.9	1.2	24.3	97.6
PWK19	19.0	6.6	11.4	0.8	18.8	98.9
PWK20	16.9	6.4	9.2	0.8	16.4	97.0
PWK24	23.0	13.7	9.1	0.7	23.5	102.2
PWK25	20.9	10.8	8.6	0.7	20.1	96.2
PWK26	17.7	8.5	7.8	0.5	16.9	95.5
PWK27	24.0	12.2	10.6	0.7	23.5	97.9
PWK28	21.0	11.0	8.9	0.9	20.8	99.0
PWK29	17.7	7.5	8.8	0.6	16.9	95.5
PWK30	23.8	15.4	7.3	0.2	22.9	96.2
PWK31	13.8	9.1	3.7	0.3	13.1	94.9
PWK32	29.0	18.8	8.4	0.4	27.6	95.2
PWK33	29.0	20.0	6.9	0.8	27.7	95.5
PWK34	20.8	13.4	5.9	0.5	19.8	95.2
PWK35	23.8	13.2	9.0	0.5	22.7	95.4
PWK36	13.7	7.0	5.6	0.4	13.0	94.9
PWK37	31.9	12.7	16.4	1.4	30.5	95.6
PWK38	17.2	9.1	6.8	0.6	16.5	95.9
PWK39	25.9	15.3	8.8	0.7	24.8	95.8
PWK41	24.0	13.0	8.9	1.0	22.9	95.4
PWK42	29.9	13.0	14.8	0.7	28.5	95.3
PWK43	29.8	12.4	16.1	0.5	29.0	97.3
PWK44	26.0	15.1	8.8	0.8	24.7	95.0
PWK45	14.4	6.6	6.7	0.4	13.7	95.1
PWK46	15.0	8.9	4.9	0.7	14.5	96.7
PWK47	22.9	12.4	9.0	0.6	22.0	96.1
PWK48	21.8	9.7	10.5	0.7	20.9	95.9
PWK49	23.9	11.0	10.9	0.8	22.7	95.0
PWK50	19.8	9.3	9.1	0.4	18.8	95.0
PWK51	21.8	15.2	5.2	0.3	20.7	95.0
PWK52	19.8	14.2	4.0	0.2	18.4	92.9
PWK55	22.0	17.9	2.8	0.4	21.1	95.9

total gas and the individual gaseous components produced during the fast pyrolysis of the maple at temperatures between 650 and 800 °C are given in Tables 19 to 22. The total gas, total liquid (inc. product water and organics), and char (solid carbonaceous residue plus ash) are plotted as a function of residence time in Figures 24 to 27. The curves follow the general trends reported for cellulose and poplar in that the total gas and principal gaseous components approach a maximum asymptotic yield while the liquids approach an asymptotic minimum value, as the reactor residence time is increased at each constant temperature investigated. The plots of the individual gas components as a function of residence time have been included in Appendix 14.6.

The asymptotic yield of total gas increases from 33 to 59 percent by mass of the maple feedstock as the temperature is increased from 650 to 800 °C. Over this same temperature range the asymptotic yields of hydrogen, carbon monoxide and carbon dioxide increase from 0.1 to 0.8, 19 to 36 and 7.1 to 9.2, respectively. Corresponding values for ethylene, total unsaturates and total hydrocarbons are 1.2 to 3.6, 2.0 to 5.0 and 4.8 to 10.3 percent, respectively.

The total liquid yields from red maple, as illustrated in Figures 24 to 27, are taken as the difference between the total maple feedstock mass and the mass of total gases plus char. This procedure of determining liquid yields was reasonable since the gases and char were measured directly with no losses and since the char was found to be constant (i.e. independent of reactor residence time) at

TABLE 19. RED MAPLE PYROLYSIS EXPERIMENTS (650°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
21	254	24.4	0.1	14.3	5.9	1.0	0.4	-	1.3	0.3	1.2
22	247	23.1	-	13.3	6.2	0.8	0.4	-	1.3	0.2	0.8
24	425	23.9	0.1	13.8	5.8	1.0	0.6	0.1	1.3	0.2	1.0
25	210	20.0	-	11.8	5.0	0.8	0.4	-	0.9	-	0.8
26	1147	33.8	0.2	20.1	7.5	1.2	0.7	0.1	-	0.3	1.3

TABLE 20. RED MAPLE PYROLYSIS EXPERIMENTS (700°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
1	125	29.4	0.1	17.9	6.5	1.3	0.5	0.4	1.4	0.4	1.3
2	174	32.2	0.1	19.7	6.7	1.4	0.6	0.4	1.7	0.4	1.4
3	262	36.0	0.2	22.0	6.9	1.6	0.7	0.5	2.2	0.5	1.6
5	367	41.2	0.3	25.3	7.9	2.0	0.8	0.5	2.5	0.5	1.7
6	368	44.0	0.3	26.9	8.5	1.9	0.8	0.5	2.9	0.5	1.8
7	173	39.9	0.3	23.8	8.4	1.7	0.7	0.5	2.4	0.5	1.8
8	89	25.9	0.1	15.0	6.4	0.9	0.5	0.4	1.4	0.4	1.1
9	245	31.3	0.1	19.4	6.0	1.4	0.6	0.3	1.8	0.3	1.4
19	87	22.0	-	13.2	5.0	0.9	0.4	0.4	1.2	0.4	0.9
27	780	44.1	0.4	26.5	8.6	1.9	0.9	0.4	3.2	0.4	1.5

* B/T - benzene/toluene

TABLE 21. RED MAPLE PYROLYSIS EXPERIMENTS (750°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
10	403	54.4	0.6	33.6	9.0	3.1	1.0	0.4	3.9	0.6	2.1
11	180	42.5	0.4	22.9	8.0	2.1	0.8	0.3	2.8	0.5	1.8
12	96	39.6	0.2	23.9	8.2	1.8	0.7	0.3	2.2	0.6	1.8
13	92	39.9	0.3	24.2	8.1	1.9	0.7	0.3	2.0	0.7	1.8
14	174	43.5	0.5	26.7	7.8	2.2	0.7	0.3	2.7	0.6	2.0
15	379	54.5	0.6	33.8	8.9	3.1	1.0	0.4	3.8	0.6	2.4

TABLE 22. RED MAPLE PYROLYSIS EXPERIMENTS (800°C): DATA SUMMARY

RUN NO.	RESIDENCE TIME (ms)	PRODUCT MASS YIELD (%)									
		Gas	H_2	CO	CO_2	C_2H_4	C_3H_6	C_2H_2	CH_4	C_2H_6	B/T*
16	358	58.8	0.8	36.0	9.3	3.7	0.8	0.6	4.6	0.6	2.4
17	183	56.6	0.4	34.8	9.4	3.6	0.8	0.7	3.5	0.9	2.3
18	99	42.2	0.3	26.2	7.0	2.6	0.7	0.5	2.7	0.6	1.7

* B/T - benzene/toluene

each temperature. The results of the mass balance (Table 23) add further credibility to the reported liquid yields. The asymptotic values of the liquid yields (representing the minimum yields at each temperature) decrease from 60 to 38 percent by mass as the temperature is increased from 650 to 800 °C as was the case with the other biomass feedstocks, the total liquid yields could be greatly increased at each temperature by reducing the residence time to a value which is lower than the asymptotic region. The maximum liquid yields measured during the maple experiments was approximately 73 percent at 650°C and 194 milliseconds. No maple experiments were conducted at residence times less than 194 ms at 650°C where higher liquid yields are likely.

Char yields were measured for all the maple experiments and were found to be dependent on reactor temperature but independent of the reactor residence times (as was the case for poplar experiments). As illustrated in Figures 24 to 27, the char yields decrease rapidly from 6.7 to 3.6 percent as the temperature is increased from 650 to 700 °C, and then decrease much more slowly to about 3.1 percent at 800°C.

Complete product recovery and subsequent mass balances were carried out during all of the red maple experiments, and a summary of these results is given in Table 23. If the results of experiments "RA 2" and "RA 10" are discarded (since portions of the aqueous phase product was evaporated with the acetone solvent during these two trials), then the average value of the product recovery is 97.2 percent of the maple feedstock mass. As indicated in previous discussions, the consistent deficit in the recovery is easily

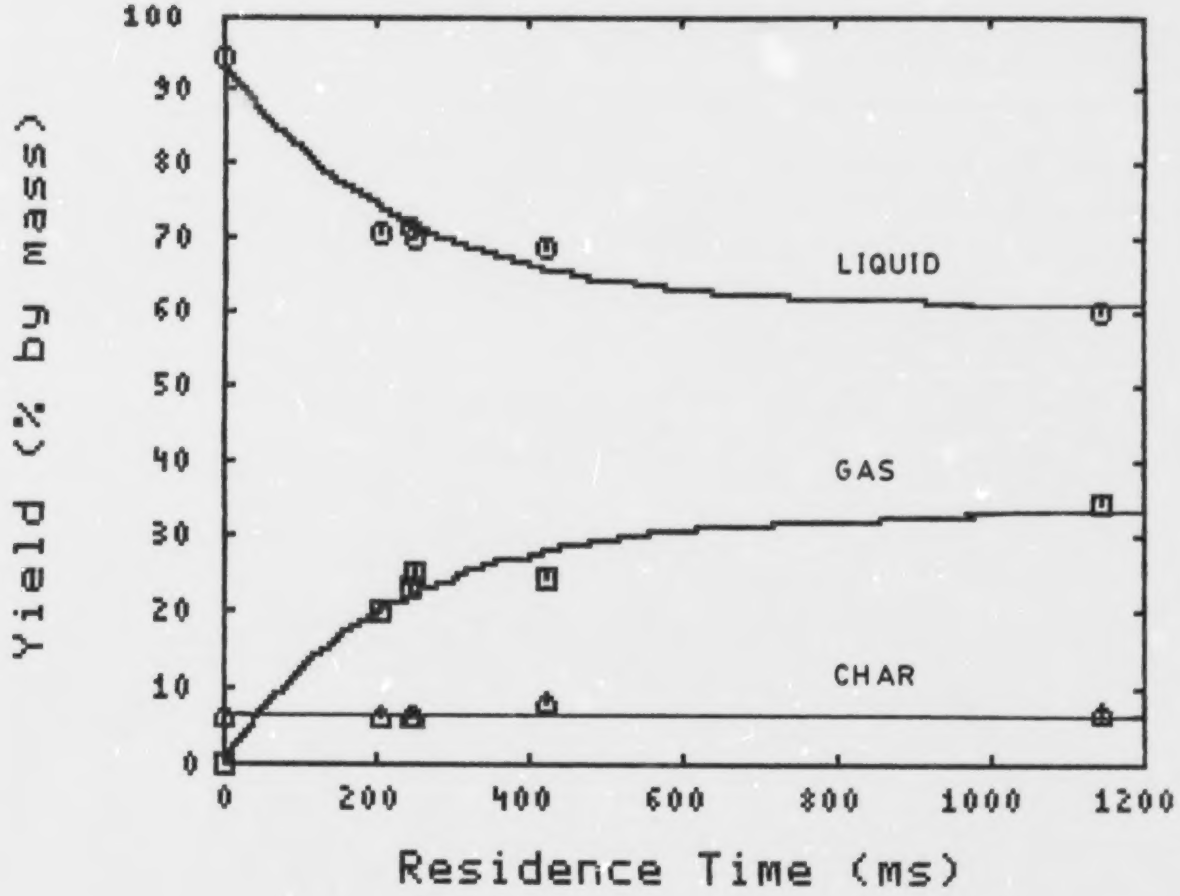


Figure 24. Fast Pyrolysis of Red Maple (650°C): Total Gas, Liquid and Char Yields vs Residence Time.

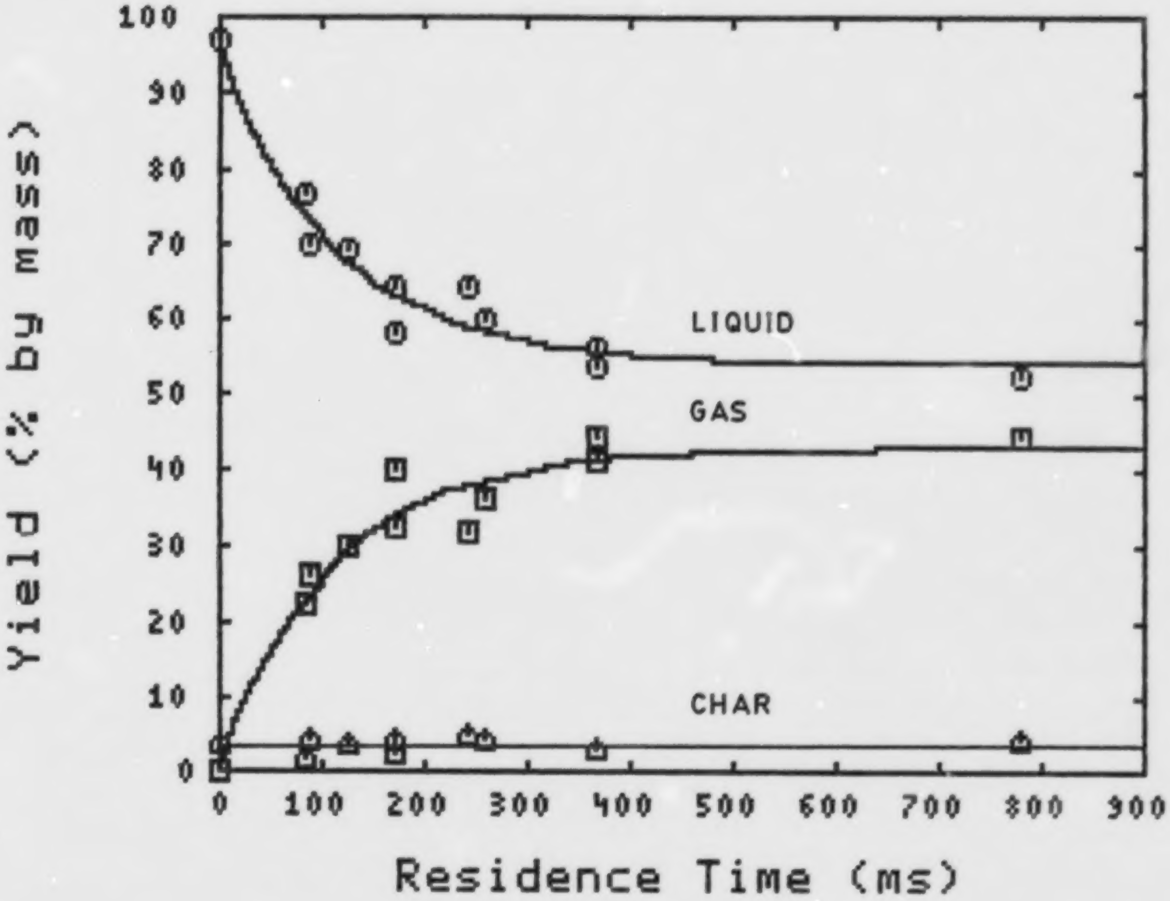


Figure 25. Fast Pyrolysis of Red Maple (700°C): Total Gas, Liquid and Char Yields vs Residence Time.

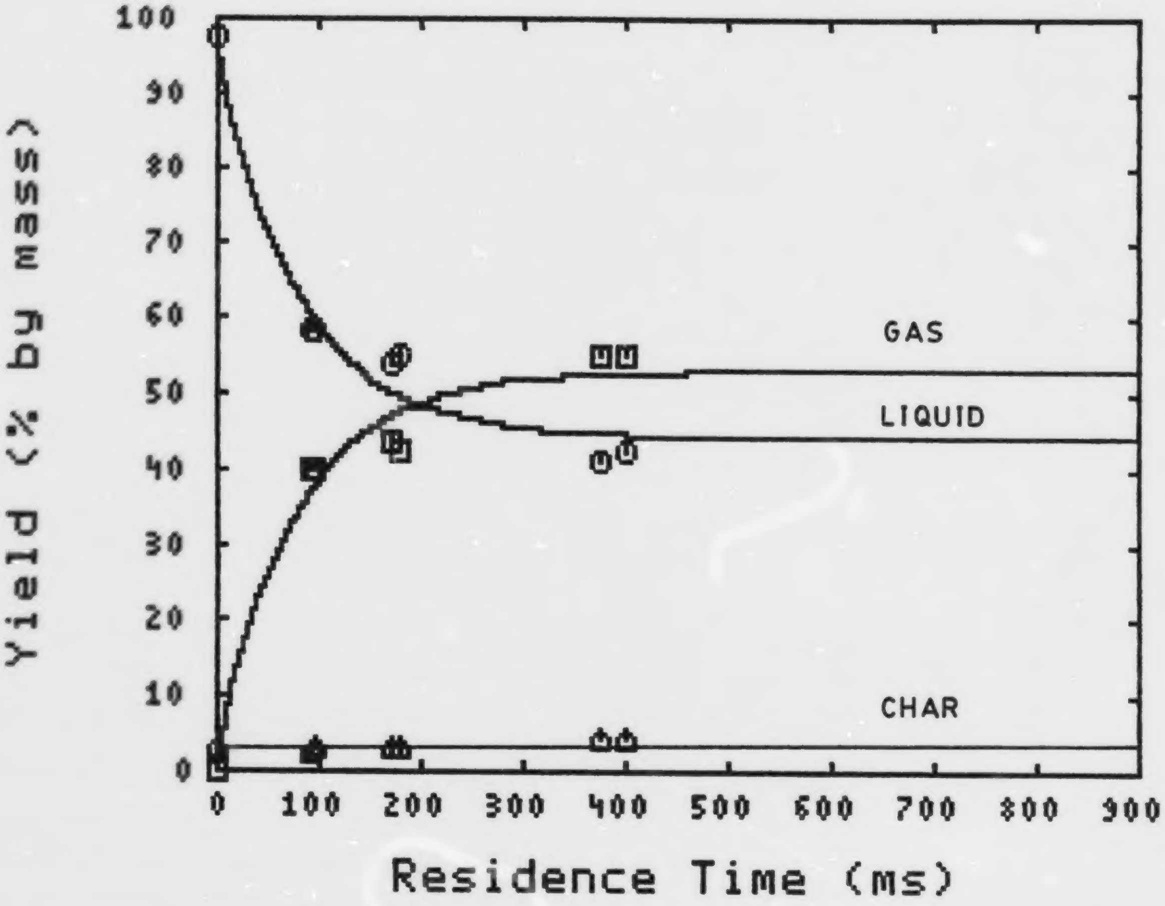


Figure 26. Fast Pyrolysis of Red Maple (750°C): Total Gas, Liquid and Char Yields vs Residence Time.

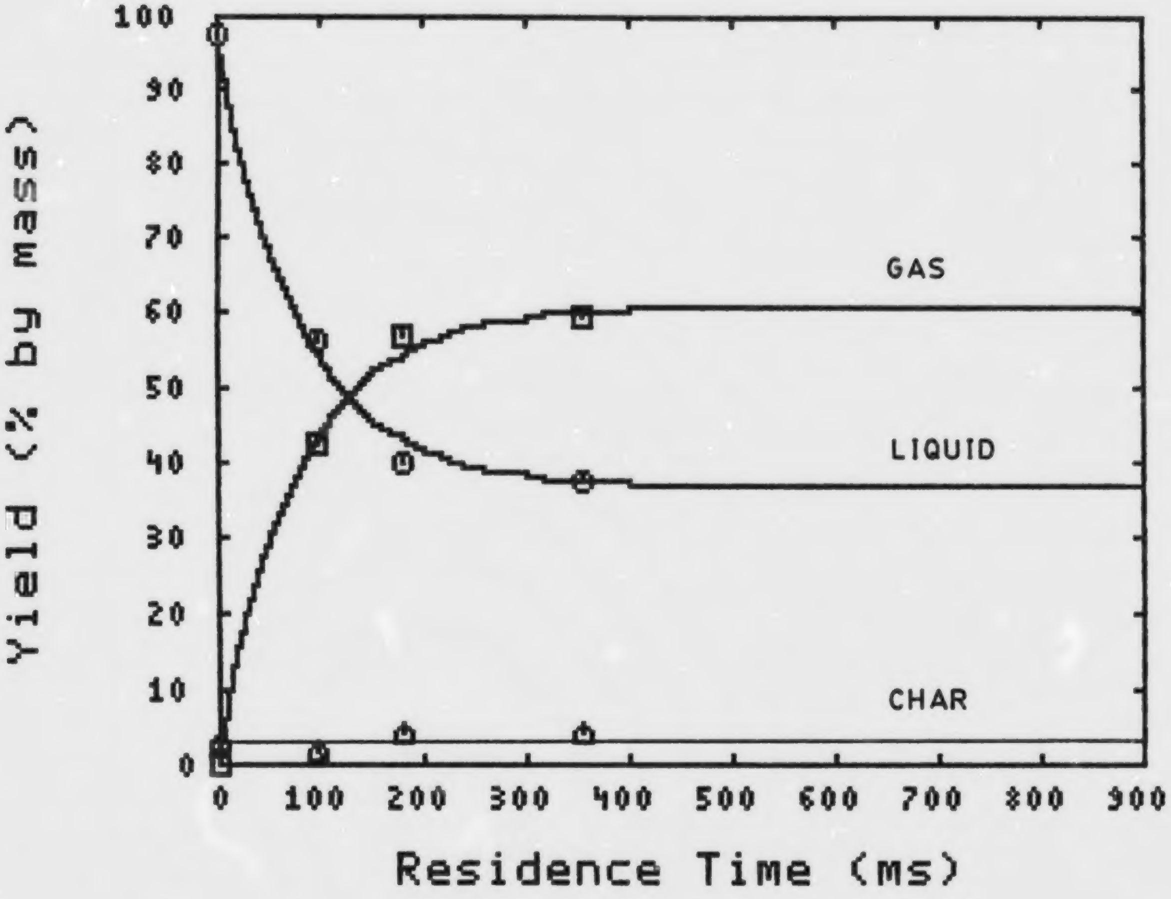


Figure 27. Fast Pyrolysis of Red Maple (800°C): Total Gas, Liquid and Char Yields vs Residence Time.

TABLE 23. RED MAPLE PYROLYSIS MASS BALANCE SUMMARY

RUN NUMBER	MAPLE FED (g)	PRODUCT RECOVERY (g)				TOTAL RECOVERY (% by mass)
		GAS	LIQUID *	CHAR	TOTAL	
RA1	41.4	12.1	25.9	1.5	39.5	95.4
RA2	36.4	11.6	20.3	1.4	33.3	91.5
RA3	48.8	17.4	28.4	2.0	47.8	98.0
RA5	31.0	12.7	16.8	0.8	30.3	97.7
RA6	50.0	21.8	25.1	1.3	48.2	96.4
RA7	34.0	13.5	19.3	0.8	33.6	98.8
RA8	44.9	11.5	30.6	1.9	44.0	98.0
RA9	57.0	17.7	34.5	2.7	54.9	96.3
RA10	70.4	37.9	20.6	2.6	61.1	86.8
RA11	32.0	13.5	17.2	1.0	31.7	99.1
RA12	29.8	11.7	16.3	0.8	28.8	96.6
RA13	39.8	15.7	21.5	0.9	38.1	95.7
RA14	66.8	28.8	32.8	2.1	63.7	95.4
RA15	47.0	25.4	18.0	2.0	45.4	96.6
RA16	63.0	36.7	26.1	2.5	65.3	103.7
RA17	22.6	12.7	8.4	0.8	21.9	96.9
RA18	29.7	12.4	15.5	0.5	28.4	95.6
RA19	19.0	4.1	13.7	0.3	18.1	95.3
RA21	26.8	6.5	18.9	1.6	27.0	100.7
RA22	43.6	10.0	29.6	2.6	42.2	96.8
RA24	34.9	8.3	22.4	2.7	33.4	95.7
RA25	35.3	7.0	23.1	3.4	33.5	94.9
RA26	38.9	13.0	22.9	2.6	38.5	99.0
RA27	66.0	28.9	32.1	2.6	63.6	96.4

accounted for by the uncondensed water vapour in the saturated carrier gas. Uncondensed vapours can be detected on the Carle gas chromatograph while water cannot be detected.

10.4 Waterloo U./U.W.O. Joint Study

During the course of the Ultrapyrolysis project, several progress meetings were held between rapid pyrolysis researchers at Waterloo University (i.e. Dr. D.S. Scott and coworkers) and those at the University of Western Ontario. These meetings were organized and chaired by the Scientific Authority, Dr. R.P. Overend. Both groups were able to achieve the rapid heating rates which are characteristic of fast pyrolysis but using different pieces of equipment. The Waterloo U. group has been conducting fast pyrolysis experiments for a number of years in a fluidized bed reactor system (using silica sands as the fluidizing medium). Since the operating temperature and residence time ranges of the Waterloo fluidized bed are 400 to 750 ^oC and 300 to 1500 milliseconds, respectively, while the corresponding ranges for the Ultrapyrolysis reactor are 650 to 900^oC and 50 to 900 milliseconds, respectively, it was apparent that there was sufficient overlap in operating conditions to attempt to get a congruent picture of rapid pyrolysis from 400 to 900 ^oC. It was therefore decided to compare the pyrolysis of identical cellulose feedstocks (Avicel) and similar wood feedstocks (red maple) in the two reactor systems with the idea of matching the Ultrapyrolysis reactor residence time (at each temperature) to that of the fluidized bed. The detailed results of the joint study have been reviewed by Dr. D.S. Scott and integrated into a paper which has been submitted for journal publication. Several portions of this paper are summarized in the following paragraphs.

The Ultrapyrolysis system and experimental procedure have been presented previously in this report. Two fluidized bed reactor systems were used at the Waterloo facilities, one was bench scale and had a capacity of about 50 grams (biomass) per hour while the second was a small pilot plant with a maximum capacity of 3 kg per hour. The pilot plant flow sheet is given in Figure 28. In the pilot plant system, dry particulate biomass is converged from a hopper by a variable speed twin-screw feeder to a discharge zone where they are picked up by a preheated transport gas and carried into the fluidized bed reactor. The reactor is wrapped with heating coils such that heat can be added selectively to the bed and/or freeboard spare as desired. Pyrolysis products are swept from the reactor to a cyclone where the particulate char and ash (if present) are separated from the product gases and vapours. The gas product and vapours are then piped to two condensers in series, the first of which is a "warm" condenser while the second uses ice water as the condensing medium. The gas passes from the condensers through a series of filters to remove residual aerosols.

After a fluidized bed experiment, the condensers are washed with acetone, the solution is filtered and the acetone is evaporated under vacuum to yield the liquid fraction. Additional liquids are collected in the filters which are weighed before and after the experiment. All

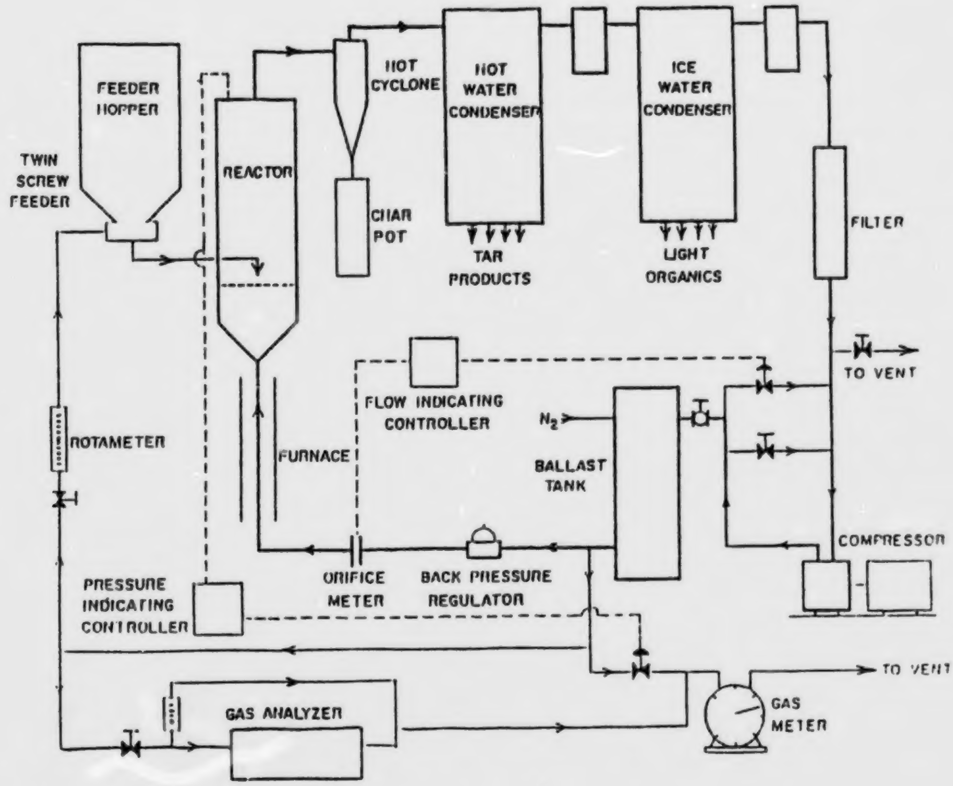


Figure 28. Waterloo University Fluidized Bed Pilot Plant Flow Scheme.

liquid products are readily soluble in acetone. The char, which is very reactive and can easily react with air when hot, is carefully collected from the acetone. The char, which is very reactive and can easily combust with air when hot, is carefully collected from the char pot and weighed. The residue from the acetone extraction which is not soluble, is included in the char fraction. Gases are analyzed for CO and CO_2 by one-line IR analysis, and complete off-line gas analysis of selected samples is accomplished using gas chromatography.

The pyrolysis experiments in the fluidized beds were all carried out at gas residence times of 450 to 550 milliseconds. For all temperatures above 650°C, this corresponds to the asymptotic product yields in the Ultrapyrolysis transport reactor. As reported previously in this report, the asymptotic region corresponds to a range of residence times where gas yields in the transport reactor rise to a maximum, liquid yields drop to a minimum, and the yields of both remain independent of reactor residence time. Accordingly, data from this region was compared to the data from the fluidized bed reactor.

The results of pyrolysis experiments using Avicel cellulose are shown in Figure 29 to 33. All yields are expressed as a percent (by mass) on a dry feed basis. Figure 29 illustrates that the yields of gas, liquids and char from two different reactor systems operated by two different research groups, are in very close agreement over the temperature range of 450 to 900 °C. This good agreement is also evident for the yields of carbon monoxide, (Figure 30), carbon dioxide

(Figure 31), methane (Figure 32) and unsaturates (i.e. ethylene and acetylene; Figure 33).

The yields of liquids, gases and char from pyrolysis experiments using red maple wood over a temperature range of 400 to 800 °C are shown in Figure 34. Although the data from the two reactor types does not overlap quite as smoothly as was the case for the cellulose experiments, the curve does confirm essential agreement of the two data sets. Figure 35 illustrates the yields of carbon monoxide and carbon dioxide as a function of temperature, while Figure 36 shows the yields of methane and unsaturates (i.e. ethylene and acetylene). Again, the agreement of data from the two types of reactors is very satisfactory.

The data for liquid yields shown in Figures 29 and 34 refer to total condensibles, that is, organic compounds plus product water formed. Product water is variable and tends to increase with temperature, so that the actual organic liquid yield decreases more rapidly than indicated by the decreasing total liquid yield in Figures 29 or 34. An optimum total liquid yield from maple of about 84 percent is apparent at approximately 500°C. The occurrence of an optimum is in general agreement with previous results from the fluidized bed using other wood feedstocks. However, this optimum is not observed for the cellulose experiments over the temperature range studied where the liquid yields continue to increase to about 92 percent as the temperature decreases to the lowest value of 450°C.

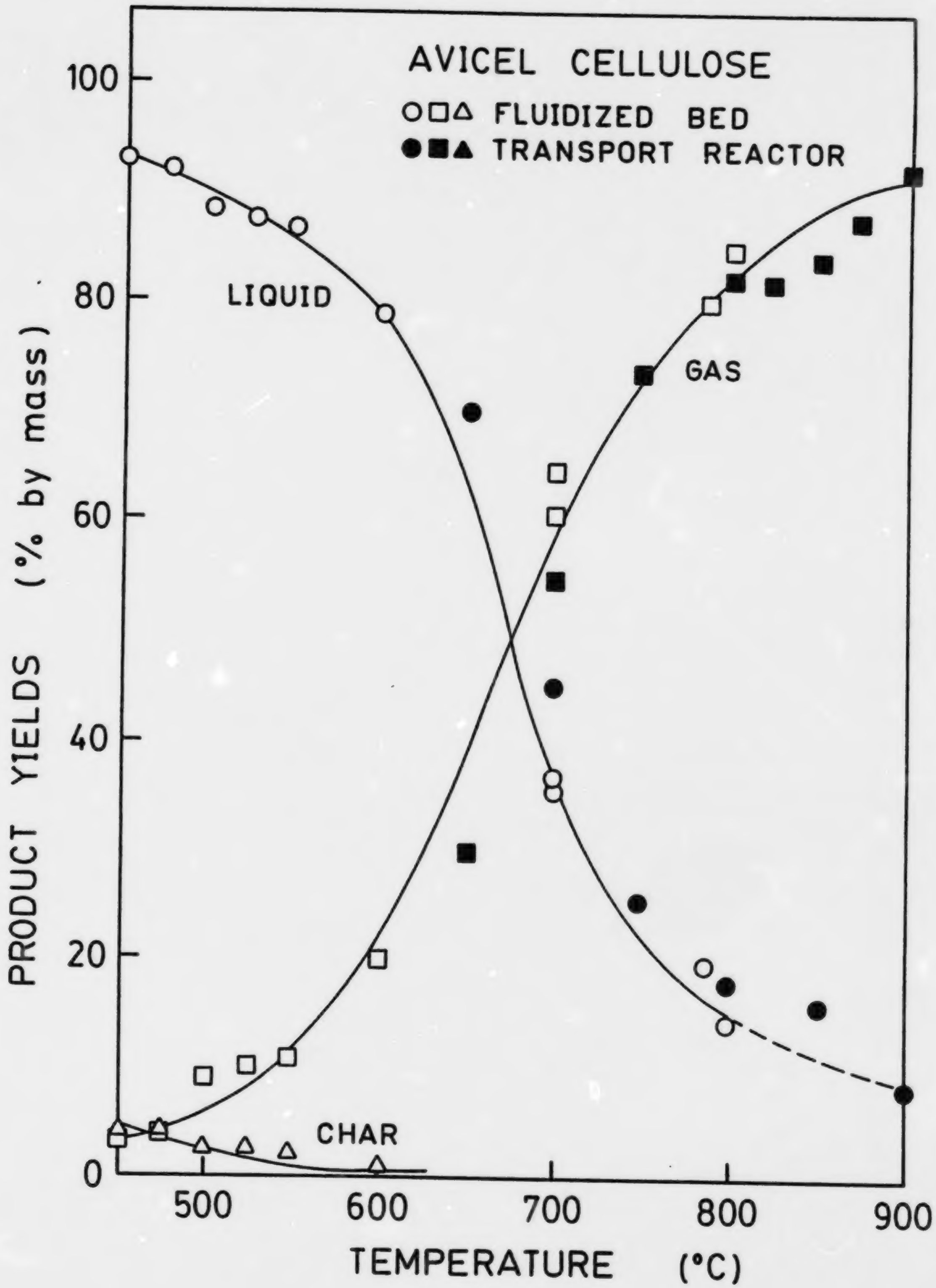


Figure 29: Fast Pyrolysis of Cellulose: Product Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems.

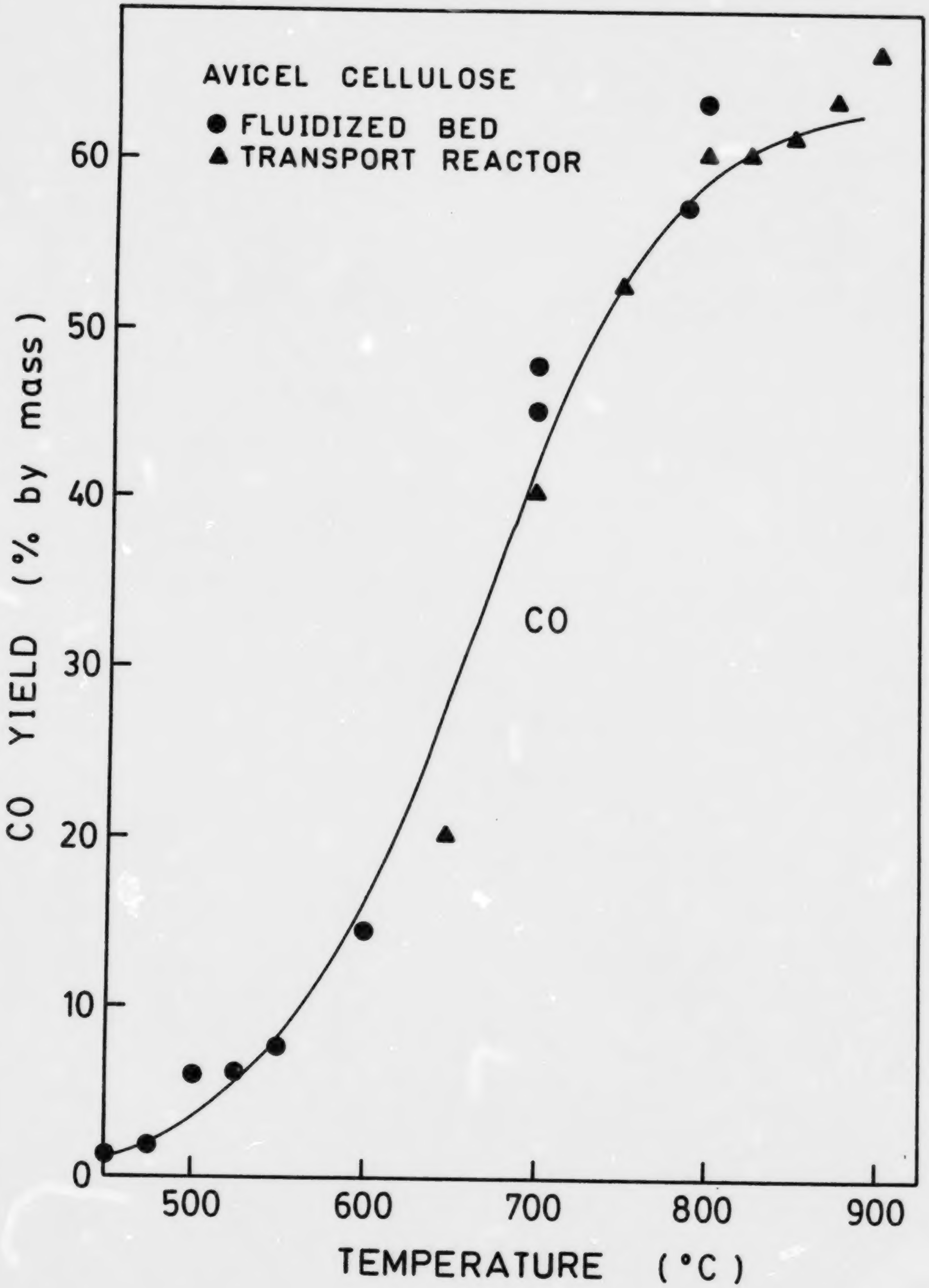


Figure 30. Fast Pyrolysis of Cellulose: Carbon Monoxide Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems.

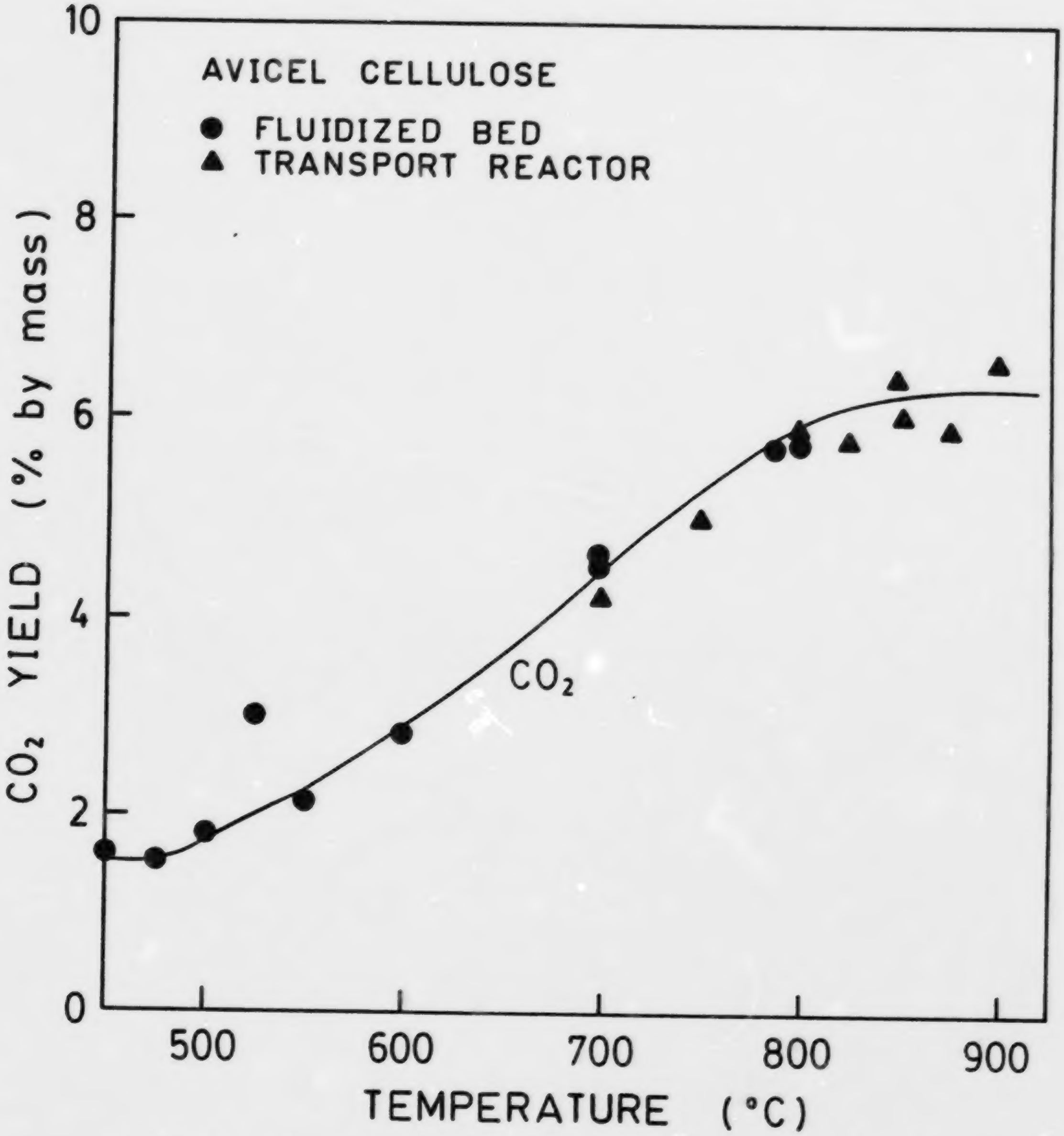


Figure 31. Fast Pyrolysis of Cellulose: Carbon Dioxide Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems.

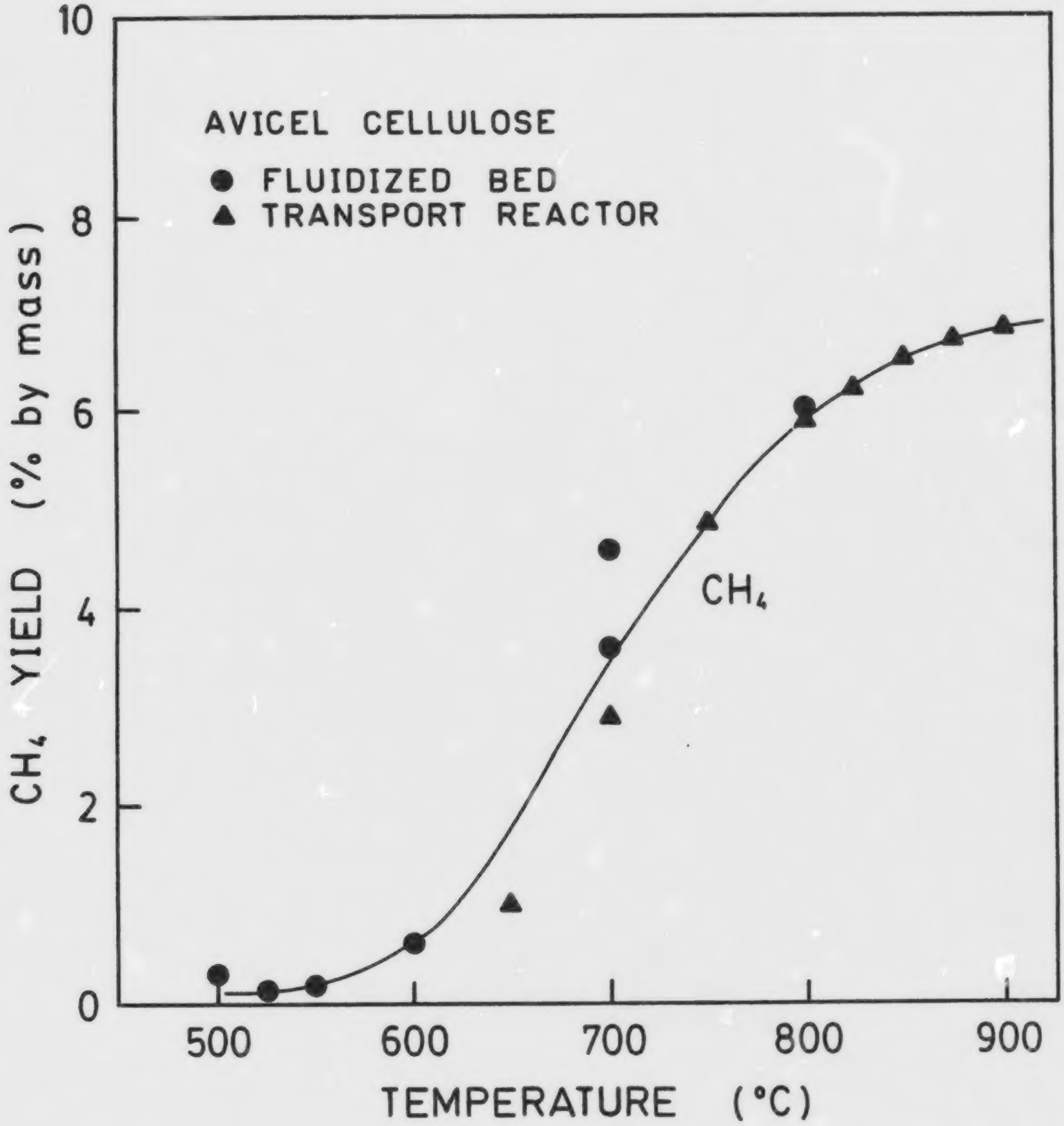


Figure 32. Fast Pyrolysis of Cellulose: Methane Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems

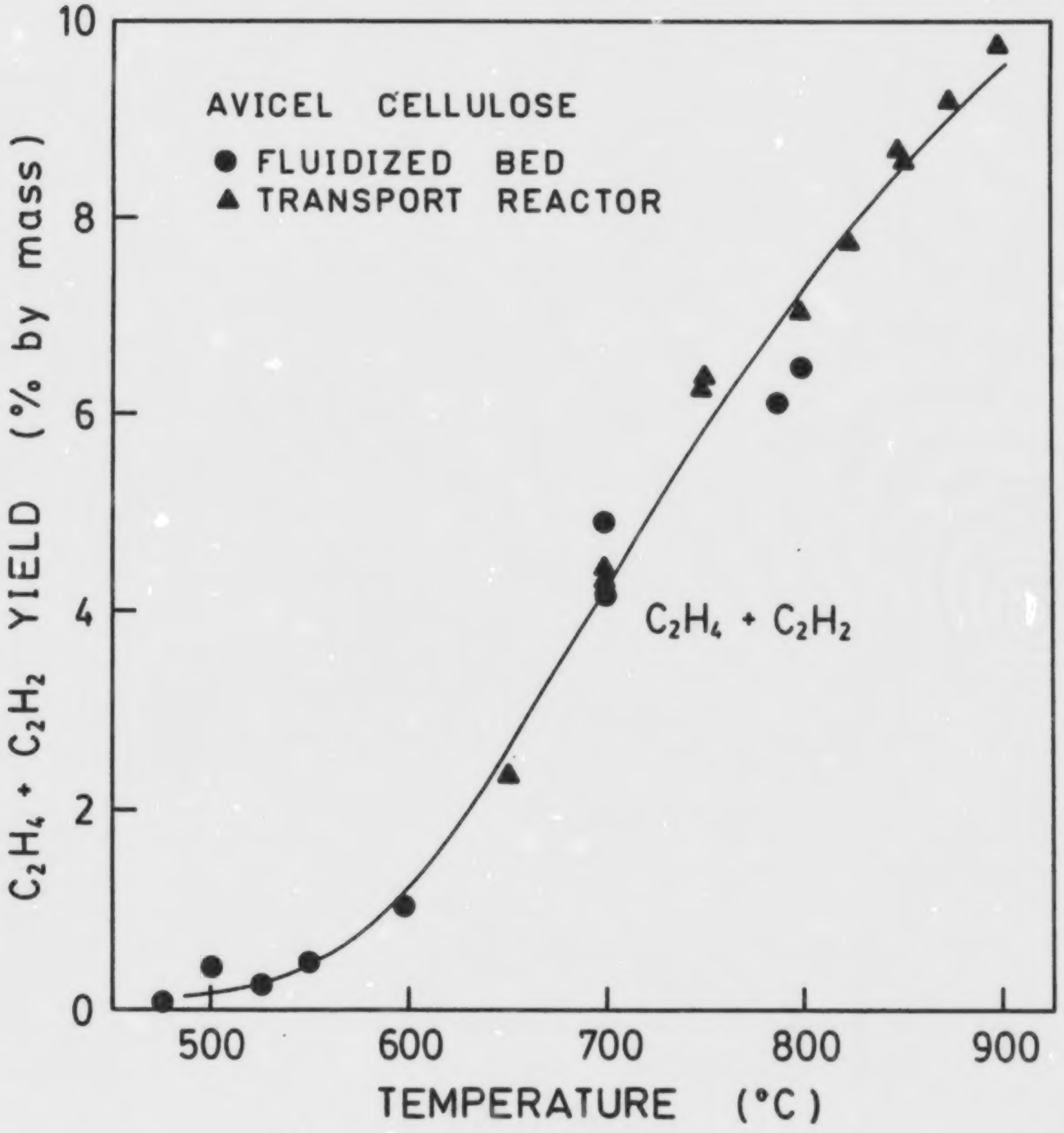


Figure 33. Fast Pyrolysis of Cellulose: Ethylene plus Acetylene Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems.

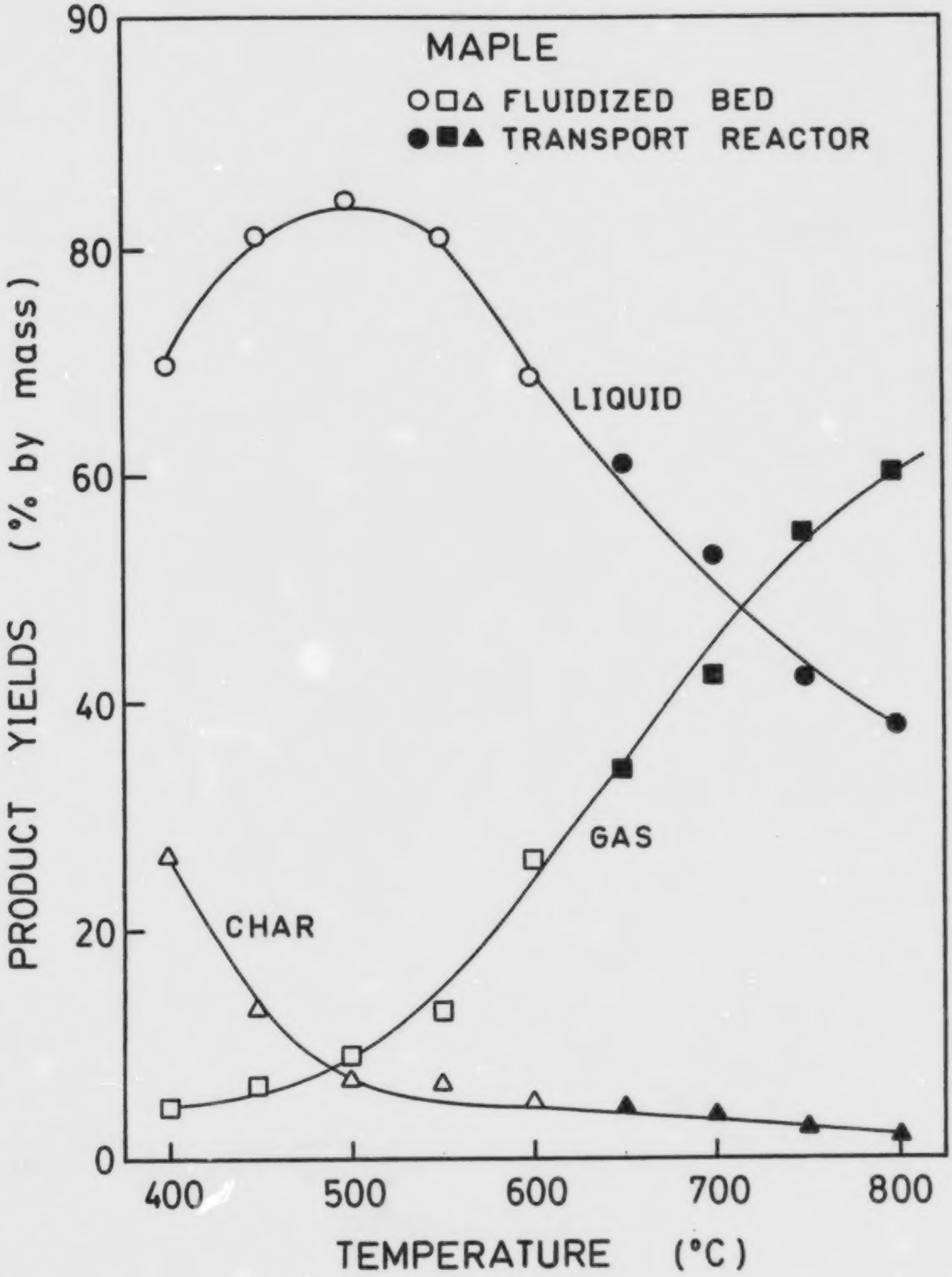


Figure 34. Fast Pyrolysis of Red Maple: Product Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems.

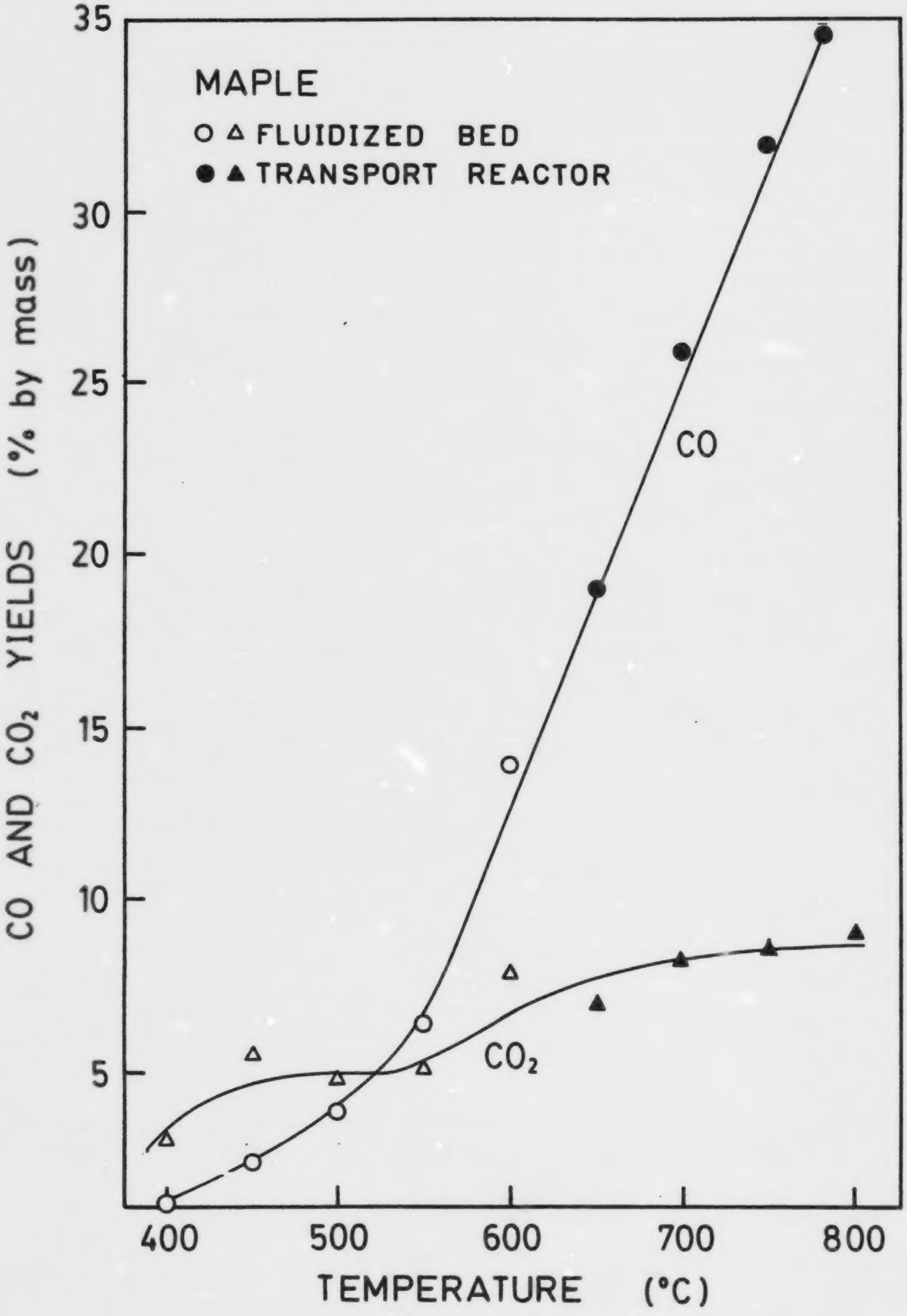


Figure 35. Fast Pyrolysis of Red Maple: Carbon Monoxide and Carbon Dioxide Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems.

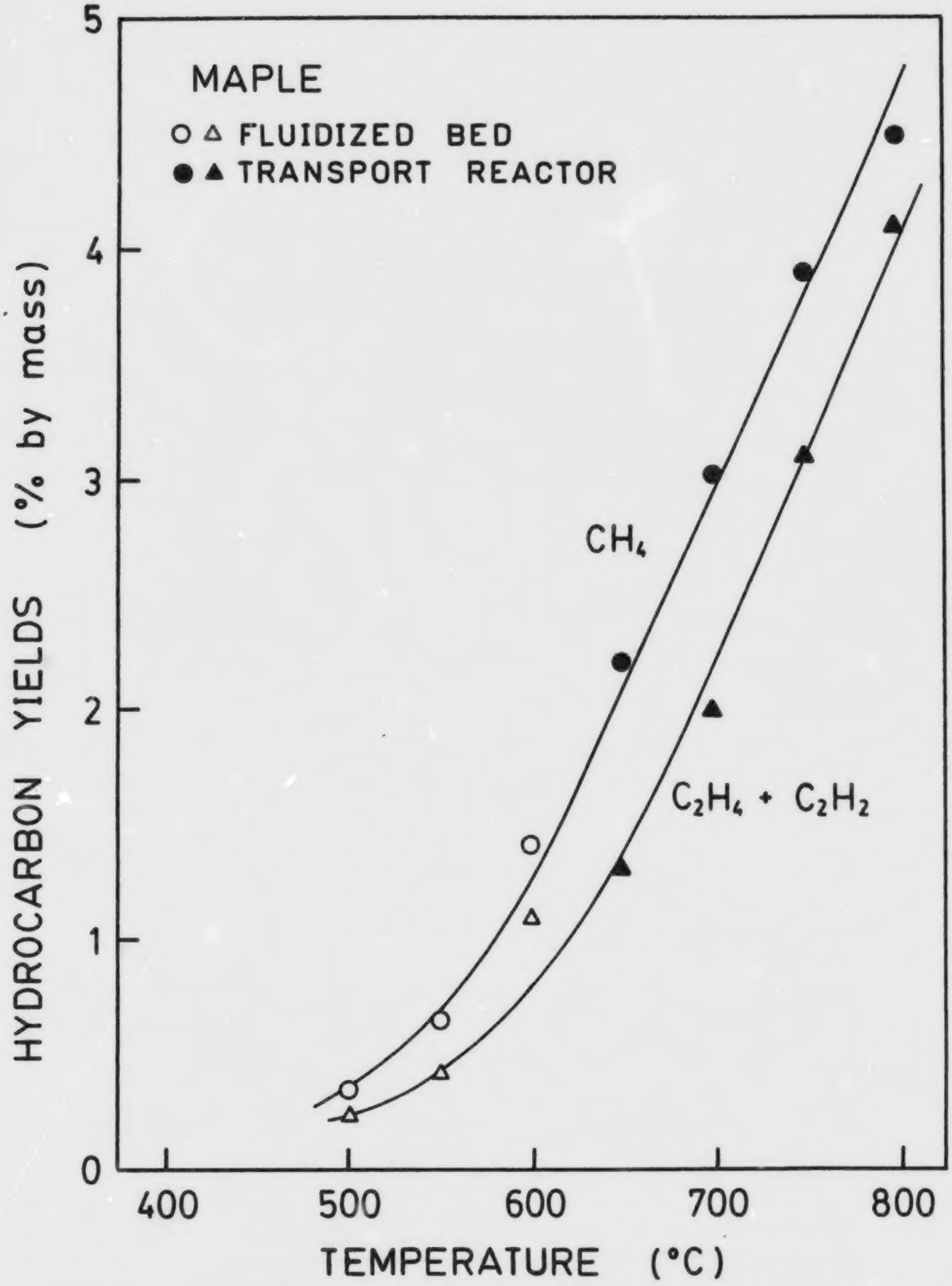


Figure 36. Fast Pyrolysis of Red Maple: Ethylene plus Acetylene and Methane Yields from the Waterloo Fluidized Bed and U.W.O. Transport Reactor Systems.

Total gas yield for the cellulose is essentially the inverse of the liquid yield, with negligible char yields except at the lowest temperatures (i.e. 4 percent at 450°C). Char yields from wood decrease rapidly from about 27 to 7 percent as the temperature increases from 400 to 500°C. From 500 to 800°C the char yield decreases much more slowly to less than 3 percent.

The results shown in Figures 29 to 36 represent experiments done in two fluidized bed reactors (bench scale and pilot plant) and in a transport reactor. Further, the experiments were done by various workers over a period of time. The agreement of all the results has implications for fast pyrolysis processes where heat transfer is not a rate limiting factor.

10.5 Hydrocarbon/Cellulose Pyrolysis

Upon completion of the cellulose experiments and after a general review of the biomass and pyrolysis kinetics literature, it was decided to initiate a brief study using ethane and methane gases in the Ultrapyrolysis system. The objectives of this study were twofold. The primary goal was to determine whether methane or ethane addition (termed "doping" for convenience) during cellulose pyrolysis would synergistically enhance the product distribution (with particular attention to ethylene yields). If this phenomenon was observed, it would presumably occur by a free-radical mechanism. The secondary goal was to observe the pyrolysis of pure ethane in the Ultrapyrolysis system, and subsequently to compare the observed decomposition kinetics with the theoretical and empirical cracking kinetics which are well characterized for this gas in the literature. In this manner, the integrity of the Ultrapyrolysis reactor system (with respect to its approach to plug flow conditions, and the accuracy of both temperature and residence time measurements) could be assessed. As a matter of good experimental practice, pure methane and ethane (i.e. in the inert nitrogen carrier gas) were to be pyrolyzed alone in the system simply as a control for the "doped" cellulose pyrolysis experiments.

The selection of methane as a cellulose "dopant" was a consequence of earlier work by Steinberg and Fallon [64,160]. Using assorted biomass and other carbonaceous feedstocks, they conducted pyrolysis experiments in an entrained tubular reactor operating at high temperatures (825 to 900°C), moderate pressures (400 to 700 kPa) and moderate vapour residence times (approximately 10 seconds). Methane was found to promote ethylene production, and a free-radical mechanism was suggested. Sundaram [16], using the same apparatus, later confirmed these enhanced ethylene yields.

The pyrolysis or cracking of pure methane or methane in inert atmospheres has been studied by a number of researchers [162,163,164], and an excellent summary has been prepared by Khan and Crynes [165]. The majority of experiments were carried out at temperatures exceeding 1000°C since methane cracking is negligible at lower temperatures and short residence times due to its refractory nature.

The pyrolysis of ethane is the primary reaction for the commercial production of ethylene. Accordingly, the kinetics are well understood and the free-radical mechanisms have been well documented [20,30, 166,167,168,170-172]. It is beyond the scope of this report to present an exhaustive review of the free-radical mechanism. However, appropriate rate equations and kinetic constants from the literature [173-175] are given due to their relevance to the observed Ultrapyrolysis kinetics.

Minor modifications were made to the Ultrapyrolysis system prior to the methane/ethane experiments. Rotameters were installed, calibrated by direct methods and integrated into the existing reactor system. The ethane and methane gases were procured from the Linde company as C.P. grade specialty gas (group 2). The methane sample was 99.27% pure with the remaining 0.73% being ethane, while the ethane was 98.91% pure and had two principal impurities - carbon dioxide at 1.05% and methane at 0.04%.

Methane or ethane were fed to the reactor system and mixed with the inert nitrogen heat carrier at a dilution (i.e. concentration) which approached that of the corresponding gases produced during cellulose pyrolysis alone. In this manner, the quantity of "dopant" gas would not overwhelm the quantity of the corresponding product gas, or vice versa, thereby making detection of cumulative or synergistic effects difficult. In other words, the quantity of methane or ethane added during an experiment was similar to the amount of methane or ethane which would be expected to be produced from the cellulose pyrolysis reactions.

Experiments were conducted at 750 and 850°C with residence times between 100 and 520 milliseconds. The two "pure" gases were pyrolyzed independently and then individually with Avicel cellulose. Methane cracking was not expected to occur to any great extent due to the strength of the carbon-hydrogen bonds, but the literature review suggested that some synergistic effects might be expected when methane is pyrolyzed with the cellulose. The ethane cracking literature, however, suggested that ethane decomposition would occur and exhibit first-order or three-halves order kinetic behaviour.

The results of the pyrolysis of methane at 750 and 850°C are given in Table 24. It is apparent from these results that the product distribution is identical to the composition of the feedstocks (i.e. methane with ethane impurity), and methane is therefore not reacting in the Ultrapyrolysis system over the investigated range of reactor residence times and temperatures. In addition, a preliminary investigation (i.e. two experiments) of methane pyrolysis at 900°C showed that about one percent of the methane had "cracked" to ethylene and hydrogen after a residence time of 1.4 seconds. These results are consistent with the literature [165] which reports that methane cracking is not significant even at 950°C unless the residence times are on the order of several seconds up to a minute. Cracking is significant on a residence time scale of tens to hundreds of milliseconds and tens to hundreds of microseconds as reaction temperatures approach 1200°C and 2000°C, respectively.

TABLE 24. METHANE AND ETHANE PYROLYSIS EXPERIMENTS: DATA SUMMARY

RUN NO.	HYDROCARBON FEEDSTOCK	TEMPERATURE (C)	RESIDENCE TIME (ms)	PRODUCT DISTRIBUTION (molar %)*							
				H2	CO2	C2H4	C2H6	C2H2	CH4	C3H6	BENZ.
MK2	Methane	850	474	-	-	-	0.3	-	99.7	-	-
MK3			154	-	-	-	0.4	-	99.7	-	-
MK5			107	-	-	-	0.2	-	99.8	-	-
MK7			107	-	-	-	0.4	-	99.6	-	-
MK8			153	-	-	-	0.6	-	99.4	-	-
MK9			390	-	-	-	0.2	-	99.8	-	-
MK10	Methane	750	511	-	-	-	0.4	-	99.6	-	-
MK11			426	-	-	-	0.5	-	99.5	-	-
MK12			169	-	-	-	-	-	100.0	-	-
MK13			116	-	-	-	-	-	100.0	-	-
MK14			116	-	-	-	-	-	100.0	-	-
MK15			169	-	-	-	-	-	100.0	-	-
EK1	Ethane	850	153	20.6	0.4	23.7	54.3	-	1.1	-	-
EK2			152	21.4	0.4	24.1	53.3	-	0.8	-	-
EK3			103	16.9	0.4	22.8	59.9	-	0.6	-	-
EK4			103	17.1	0.4	21.9	59.9	-	0.6	-	-
EK5			385	35.7	0.5	35.2	26.2	0.5	1.9	0.1	0.1
EK6			459	37.1	0.6	35.7	23.9	0.5	1.1	-	-
EK20			271	30.5	0.5	30.5	36.5	0.2	1.4	0.1	0.1
EK24			173	26.4	0.7	32.7	39.0	0.3	1.1	-	-
EK25			200	28.5	0.6	34.1	35.2	0.3	1.3	-	-
EK7	Ethane	750	424	4.9	0.9	10.0	84.0	-	0.3	-	-
EK8			511	6.2	1.0	11.5	81.3	-	-	-	-
EK10			111	2.4	0.9	2.4	96.7	-	-	-	-
EK11			164	3.2	1.0	3.2	95.9	-	-	-	-
EK12			112	2.4	0.9	2.4	96.7	-	-	-	-
EK15			167	3.1	0.9	3.1	96.0	-	-	-	-
EK16			296	5.3	0.9	5.3	93.8	-	-	-	-
EK21			422	4.4	0.5	9.3	85.8	-	-	-	-
EK22			509	5.6	0.4	10.2	83.7	-	-	-	-
EK23			298	8.4	0.6	8.4	91.0	-	-	-	-

* The molar % is expressed on a nitrogen-free basis (i.e. the inert nitrogen carrier gas is not included).

The results of the pyrolysis of ethane (which was investigated under experimental conditions which were similar to those for methane pyrolysis), are also given in Table 24. In this case, principal pyrolysis products such as hydrogen and ethylene are observed at all temperatures and residence times investigated. The presence of carbon dioxide in the product is a consequence of the impurity of the ethane feedstock gas. At 850°C, methane is a minor product at all residence times while acetylene, benzene and propylene are apparent only at the longer residence times. These minor pyrolysis products are not detected at 750°C, with the exception of methane which was detected in one of the duplicate runs at approximately 420 milliseconds. Of the primary products of ethane pyrolysis, ethylene and hydrogen are reported in the literature to predominate while minor amounts of methane are known to occur [178]. The principal secondary product is acetylene (with a proportional amount of hydrogen) with minor production of benzene, propylene, naphthalene and coke [165].

A plot of the disappearance of ethane and the appearance of primary pyrolysis products at 850°C as a function of residence time is given in Figure 37. As expected from the reaction stoichiometry, approximately equal concentrations of ethylene and hydrogen are produced. The product distribution as illustrated in Figure 37 is consistent with the widely accepted theoretical kinetic model for ethane pyrolysis known as the Rice-Herzfeld mechanism [167].

The Rice-Herzfeld model is a free-radical mechanism whose rate is first-order in ethane, and which has been experimentally verified.

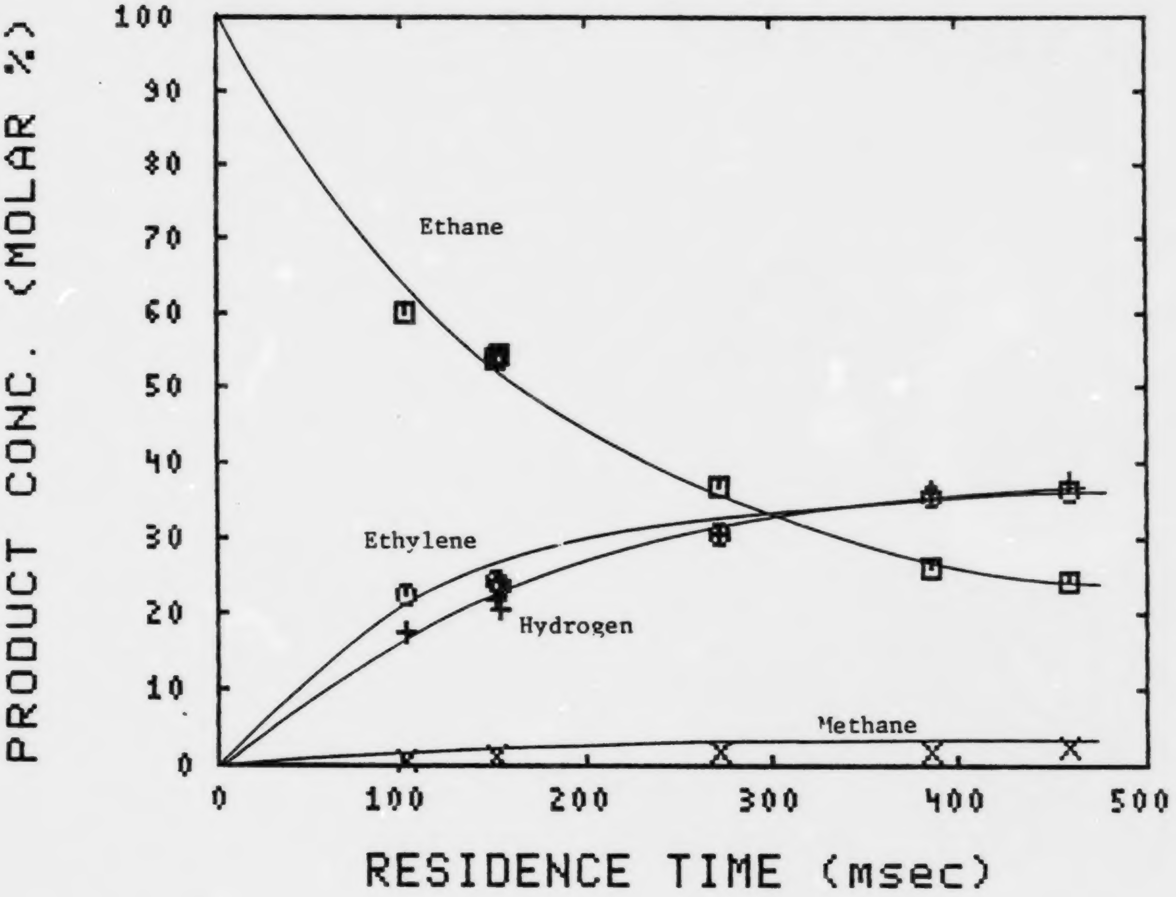


Figure 37. Ethane Pyrolysis (850 C): Ethane Disappearance and Primary Product Appearance vs Residence Time.

Therefore the empirical demonstration of first-order ethane pyrolysis kinetics in the Ultrapyrolysis system and comparable rate constants would confirm the validity of this reactor system for utility in kinetic studies. In a first-order model, a plot of the natural logarithm of the ratio of a reactant concentration at time "t" (CA) to the initial reactant concentration (CA_0) vs the residence time (t) should give a straight line. Table 25 presents a summary of the data required to generate such a plot for the pyrolysis of ethane at 750 and 850°C. The corresponding curves are given for the two temperatures in Figures 38 and 39, respectively.

The first-order plot for ethane pyrolysis at 750°C (Figure 38) is clearly linear, and the kinetics are first-order in ethane as expected. The slope, which represents the first-order rate constant, has a value of 0.39 s^{-1}. Working in a similar temperature range, Marek and McCluer [174] give the following equation for the first-order rate constant:

$$\log k = 15.12 - 15970/T$$

where T is the reaction temperature in degrees Kelvin and k is the rate constant in s^{-1}. At 750°C (1023 K), the rate constant is calculated to be 0.33 s^{-1}. The deviation of the Ultrapyrolysis value from this literature value is 18 percent. Lin and Back [175] also working at temperatures in the range of 750°C, give the following rate equation:

$$\log k = (16.22 \pm 0.11) - [(77600 \pm 600)/(2303\ RT)]$$

where T is the reaction temperature in degrees Kelvin, and k is the rate constant (1.987 cal k^{-1} mol^{-1}). At 750°C, the rate constant is

TABLE 25. FIRST-ORDER DATA FOR ETHANE PYROLYSIS AT 750 AND 850 C

RUN NO.	TEMPERATURE (C)	RESIDENCE TIME (ms)	ETHANE CONCENTRATION *		ln (Co/Ct)
			[C2H6]o	[C2H6]t	
EK7	750	424	13.2	11.0	0.182
EK8		511	15.9	12.9	0.209
EK10		111	8.2	7.9	0.037
EK11		164	12.0	11.3	0.060
EK12		112	8.2	7.8	0.050
EK15		167	12.0	11.0	0.087
EK16		296	21.2	19.0	0.110
EK21		422	13.0	11.2	0.149
EK22		509	15.7	12.9	0.196
EK23		298	9.3	8.5	0.090
EK1	850	153	10.9	7.1	0.429
EK2		152	10.9	7.0	0.443
EK3		103	7.4	5.5	0.297
EK4		103	7.4	5.5	0.297
EK5		385	11.9	4.4	0.995
EK6		459	14.5	4.5	1.142
EK20		271	19.2	8.9	0.769

* Units of concentration are (moles/liter) * E4
Initial C2H6 concentration = [C2H6]o = Co
Final C2H6 concentration (at time "t") = [C2H6]t = Ct

TABLE 26. RESULTS OF THE PYROLYSIS OF CELLULOSE IN METHANE AND ETHANE ATMOSPHERES AT 850 C

RUN NO.	PYROLYSIS ATMOSPHERE	RESIDENCE TIME (ms)	PRODUCT YIELD (% by mass)						
			Gas	H2	CO	CO2	CH4	C2H4	C2H2
CK310	Nitrogen	376	83.6	1.6	59.7	5.8	5.9	7.0	1.5
CEK1	Ethane	365	80.5	1.5	55.6	5.7	6.0	6.8	1.5
CK318	Nitrogen	328	83.6	1.6	59.7	6.0	5.7	7.0	1.6
CEK2	Ethane	324	82.0	1.6	56.8	5.9	5.5	6.9	1.4
CMK2	Methane	316	82.0	1.4	58.7	5.3	5.8	6.7	1.3
CK320	Nitrogen	130	81.2	1.5	58.0	5.8	4.8	6.6	1.5
CMK1	Methane	130	79.8	1.3	55.0	5.6	4.7	5.9	1.0
CK321	Nitrogen	106	73.1	1.3	52.6	5.1	3.9	5.9	1.4
CMK3	Methane	106	77.0	1.1	56.4	5.5	4.3	6.5	1.4

calculated to be 0.44 s^{-1}, and the range (accounting for the limits) is 0.26 to 0.76 s^{-1}. The Ultrapyrolysis value is well within this range. Overall, the first-order rate constant for ethane pyrolysis at 750°C (as estimated from the Ultrapyrolysis data) seems to be in good agreement with the literature values. This is quite remarkable since the Ultrapyrolysis system is relatively large and an error of ± 5°C in the measurement of the reactor temperature at 750°C would give a range of 0.27 to 0.39 s^{-1} for the rate constant from the Marek-McCluer equation and a range of 0.37 to 0.53 s^{-1} from the Lin-Back equation.

The first-order plot for ethane pyrolysis at 850°C (Figure 39) is also linear, thereby indicating that the kinetics are first-order in ethane as expected. The first-order rate constant (calculated from the slope of the plot) is 2.5 s^{-1}. Steacie and Shane [173] report a rate constant of 2.76 s^{-1} at 850°C. The Ultrapyrolysis value deviates from the literature value by about 9 percent. Based on the primary product distribution and the empirical kinetics of ethane pyrolysis at 850°C, the Ultrapyrolysis results are consistent with the literature.

It can be generally concluded from the results of the pyrolysis of ethane at 750 and 850°C, that the estimated time-temperature history of the Ultrapyrolysis system is not significantly different from the actual values. If the estimates of either the residence time or reactor temperature were in significant error, then the calculation of the kinetic constants would also deviate significantly from the literature values. The results confirm the "integrity" of the reactor system as a reliable tool for kinetic studies, and also provide a

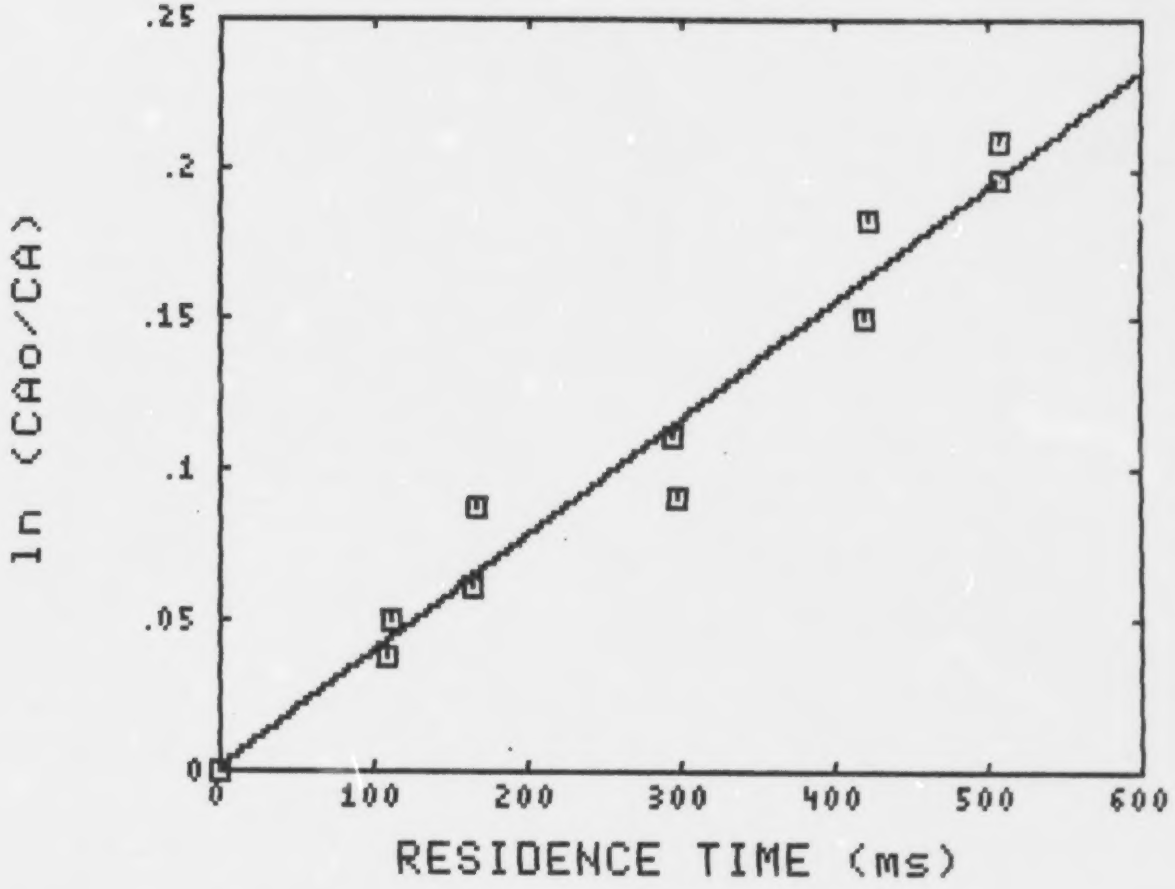


Figure 38. First-Order Plot for Ethane Pyrolysis (750 C).

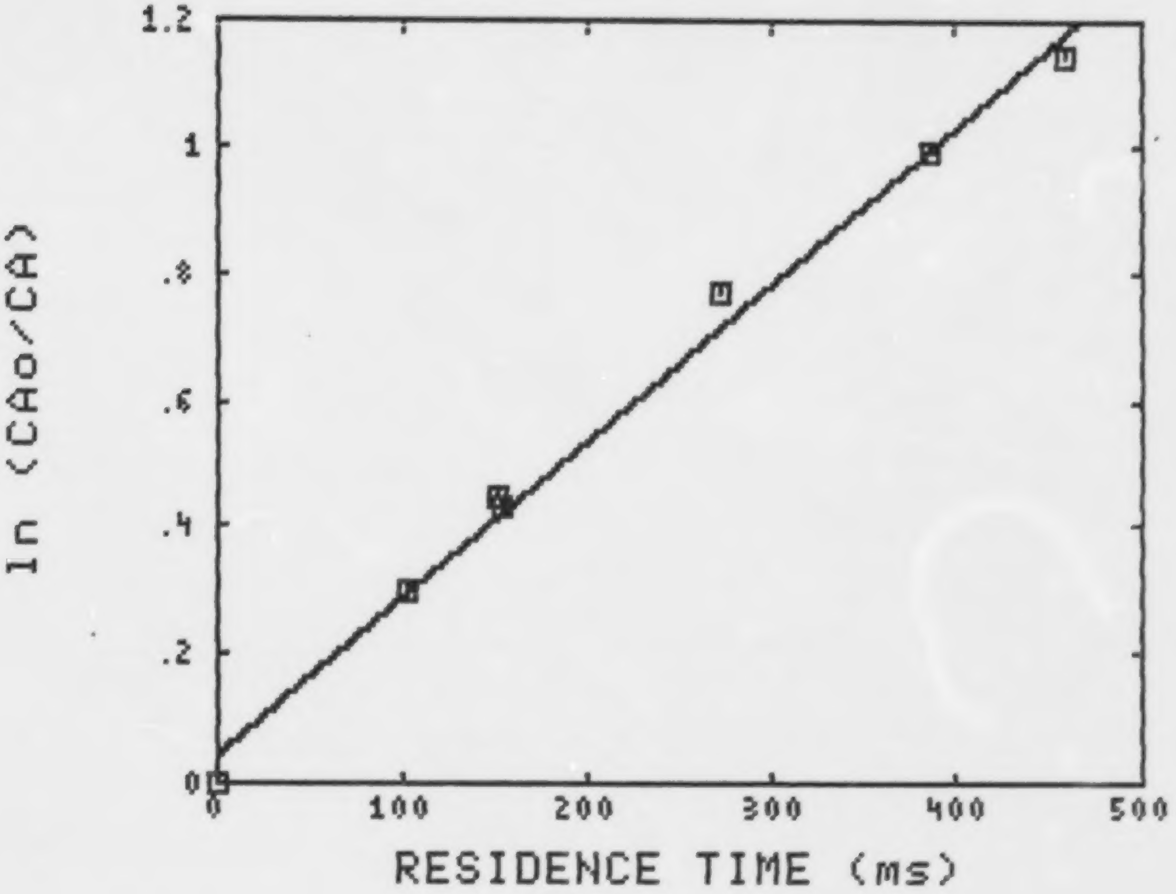


Figure 39. First-Order Plot for Ethane Pyrolysis (850 C).

basis for incorporating kinetic models for other hydrocarbons (i.e. literature models) into the cellulose Ultrapyrolysis model without actually pyrolyzing those hydrocarbons independently in the system.

The results of the pyrolysis of cellulose in methane and ethane atmosphere (i.e. diluted in inert nitrogen carrier gas) along with the corresponding cellulose control experiments (i.e. only inert nitrogen in the feedstock gas) are given in Table 26. The methane and ethane were reacted at concentrations which were similar to the concentrations used in the "pure" methane and ethane pyrolysis experiments, and these concentrations were also similar to the quantities of methane and ethane normally produced during the pyrolysis of pure Avicel cellulose. In order to clearly illustrate any synergistic effects should they be evident, the results in Table 26 have been "normalized" by subtracting the yields of products and residual reactants from the pyrolysis of pure methane (which are nonexistent) and ethane. Therefore, if the pyrolysis of combined "dopant" gas (methane or ethane) and cellulose is simply the sum of the independent pyrolysis of the dopant and cellulose, then the tabulated results should be similar. It is apparent from Table 26 and from the corresponding curves in Figures 40 and 41, that there are no detectable synergistic effects either in dilute methane or ethane atmospheres under the conditions investigated. Additional cellulose pyrolysis data are included in Figures 40 and 41, along with the formal control experiments, in order to extend the curve. Figure 40 represents the total gas yield from control and doped cellulose experiments at 850°C plotted as a function of residence time. However, Figure 41, representing the total ethylene yield at 850°C as a

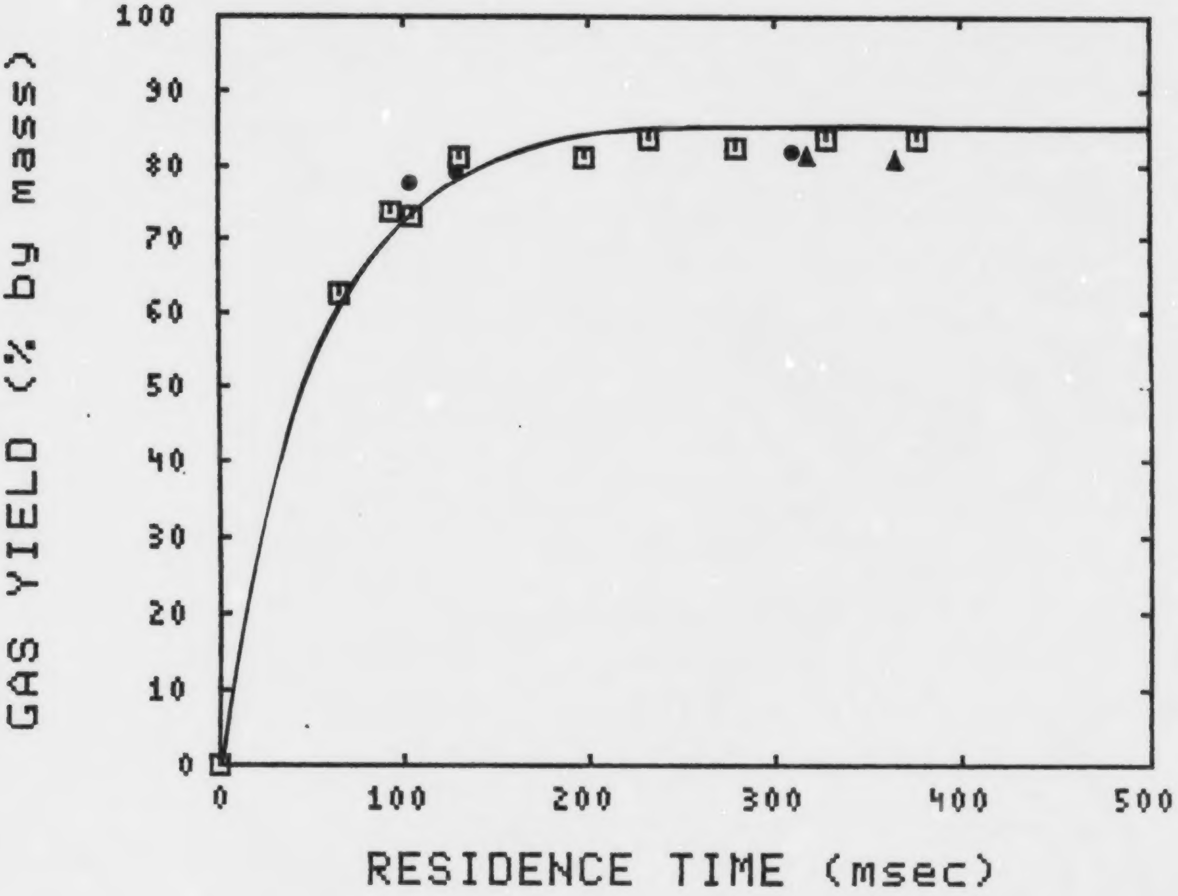


Figure 40. Pyrolysis of Cellulose in Methane (●), Ethane (▲) and Nitrogen (▣). Atmospheres at 850^{o}C: Total Gas Yield vs Residence Time.

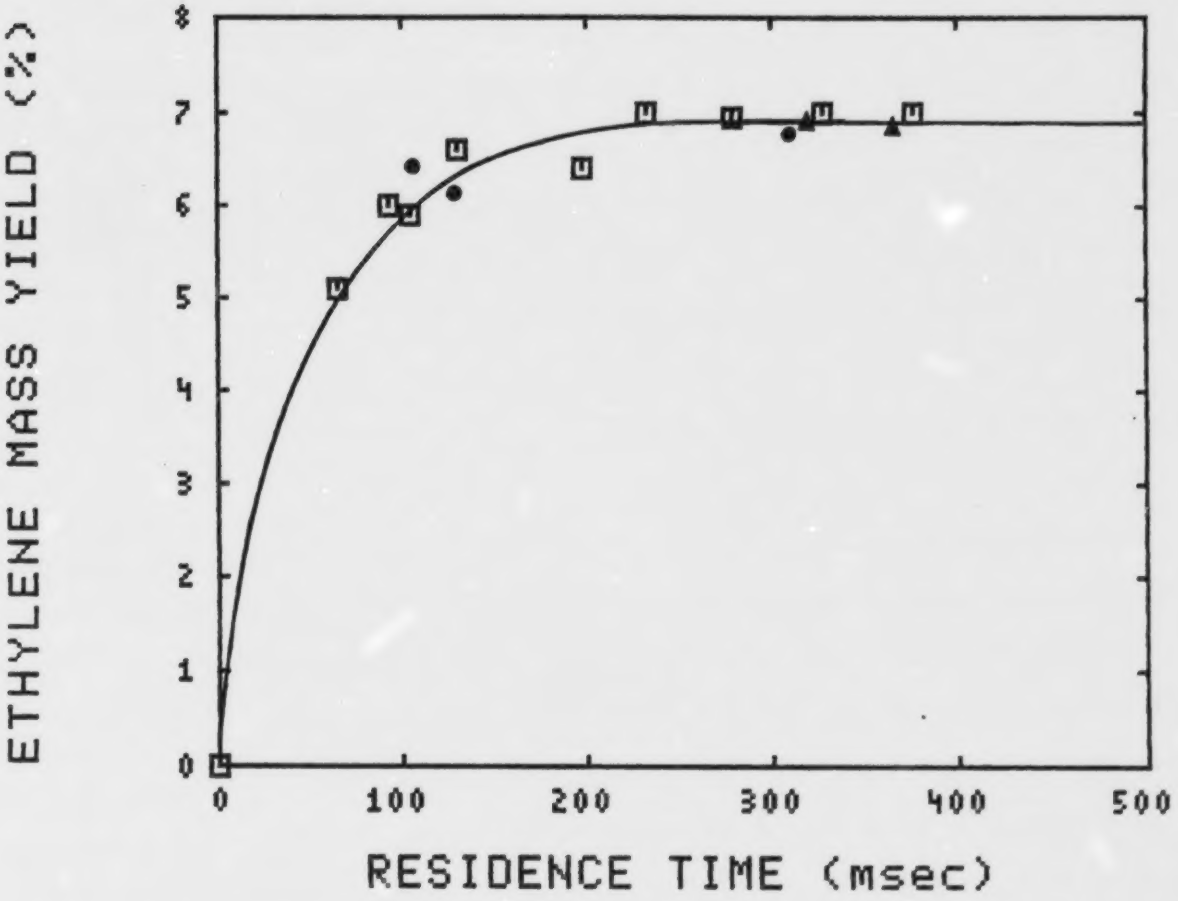


Figure 41. Pyrolysis of Cellulose in Methane (●), Ethane (▲) and Nitrogen (⊡) Atmospheres at 850 C: Ethylene Yield vs Residence Time.

function of residence time for control and doped cellulose experiments, is of more interest due to the synergism reported previously when reviewing the work of Sundaram, Steinberg and Fallon [64,160,161] in methane atmospheres. Perhaps the conditions in the Ultrapyrolysis reactor were not as severe as those reported in the above literature with respect to pressure, temperature and methane concentration. Nevertheless, enhanced yields were not apparent in any of the experiments conducted in the Ultrapyrolysis system.

10.6 Sand Thermofor Studies

It was stated previously in this report that one of the principal potential advantages of a commercial-scale Ultrapyrolysis system would be the extremely compact reactor size (i.e. low capital costs for a given plant capacity) due to the use of sand as the heat carrier. A gaseous thermofor would require a much larger volume (at similar reactor conditions) to carry an equivalent amount of heat. In addition, the heat transfer from solid particles to a solid feedstock is much more efficient than heat transfer from a gas (due to the "ablative" heat transfer), and therefore much larger biomass particles could be fast pyrolyzed in the system. In spite of these considerations, it is evident that all of the Ultrapyrolysis experiments reviewed thus far have employed only a gaseous nitrogen heat carrier. It was assumed by the Ultrapyrolysis researchers that for small particles, the fast pyrolysis product yields would be independent of the type of thermofor as long as the thermofor was chemically inert (i.e. non-reactive and/or noncatalytic). Implicit in this assumption are the following corollaries:

1. Sand thermofor is not catalytic at the temperatures, residence times and other reactor conditions under investigation during the Ultrapyrolysis program.
2. For small biomass particles such as were used in the Ultrapyrolysis experiments (i.e. 100 μm), the heat transfer is sufficient using either sand or nitrogen such that the time for the particle to heat up to reactor temperature is a fraction of the total vapour residence time.

Since nitrogen is much more convenient than sand for use in the Ultrapyrolysis apparatus and since the liquid products can be recovered much more easily, it was decided to conduct the large proportion of the experiments using nitrogen as the heat carrier.

Upon completion of the cellulose, poplar and maple feedstock experiments using nitrogen thermofor, a limited number of cellulose pyrolysis experiments using sand thermofor were conducted at a single temperature (i.e. 800°C). These were carried out to accomplish a preliminary comparison with previous nitrogen trials. A mass ratio of thermofor to cellulose of 10:1 was typically employed (reflecting the predicted ratio for a commercial design). The results of the thermofor comparison study are given in Table 27. It is important to note that all of the residence times investigated were in the asymptotic yield region at 800°C where the yields of total gas, gaseous components and total liquid remain constant over a particular range of reactor residence times.

A qualitative review of the data in Table 27 would seem to suggest that there is little or no difference associated with the type of thermofor used. The mean yields of total gas at 800°C, for example,

TABLE 27. COMPARISON OF FAST PYROLYSIS EXPERIMENTS AT 800 C USING GASEOUS (NITROGEN) AND SOLID (SAND) THERMOFOR

TYPE OF THERMOFOR	RUN NO.	RESIDENCE TIME (ms)	COMPONENT MASS YIELD (%)									
			Gas	H2	CO	CO2	C2H4	C3H6	C2H2	CH4	C2H6	B/T*
NITROGEN	CK378	390	79.1	1.7	57.4	5.3	6.1	1.1	0.8	5.3	0.5	1.1
	CK400	370	78.6	1.4	57.0	4.9	6.0	1.0	0.9	6.1	0.6	0.8
	CK401	369	80.4	1.5	57.0	5.2	6.2	1.0	0.6	5.7	0.6	0.8
	CK402	370	81.1	1.5	57.0	5.2	6.2	1.0	0.7	5.7	0.6	0.9
	MEAN VALUES		79.80	1.53	57.10	5.15	6.13	1.03	0.75	5.70	0.58	0.90
	STD. DEV'N		1.00	0.11	0.17	0.15	0.08	0.04	0.11	0.28	0.04	0.12
SAND	TS1	387	80.5	1.3	58.0	6.1	6.1	1.1	0.8	5.5	0.7	1.0
	TS2	371	82.0	1.5	59.8	5.4	6.3	1.1	0.6	5.6	0.6	1.0
	TS3	367	78.9	1.4	57.8	5.0	6.0	1.1	0.7	5.3	0.6	0.9
	TS4	367	77.1	1.3	56.5	5.2	5.8	1.1	0.5	5.2	0.5	1.0
	MEAN VALUES		79.63	1.38	58.03	5.43	6.05	1.10	0.65	5.40	0.60	0.98
	STD. DEV'N		1.82	0.08	1.18	0.41	0.18	0	0.11	0.16	0.07	0.04

* B/T - benzene/toluene

TABLE 28. SUMMARY OF T-TEST STATISTICS: GASEOUS AND SOLID THERMOFOR EXPERIMENTS AT 800 C

GAS PRODUCT	N2 THERMOFOR		SAND THERMOFOR		T - TEST RESULTS*					
					SIMILAR VARIANCE			DISSIMILAR VARIANCE		
	MEAN YIELD	STD DEV.	MEAN YIELD	STD DEV.	V	T	Tc	V	T	Tc
Total Gas	79.80	1.00	79.63	1.82	6	0.163	2.45	5	0.163	2.57
Hydrogen	1.53	0.11	1.38	0.08	6	2.205	" "	5	2.205	2.57
Carb. Monox.	57.10	0.17	58.03	1.18	6	1.560	" "	3	1.560	3.18
Carb. Diox.	5.15	0.15	5.43	0.41	6	1.282	" "	4	1.282	2.78
Ethylene	6.13	0.08	6.05	0.18	6	0.812	" "	4	0.812	2.78
Propylene	1.03	0.04	1.10	0	6	3.499	" "	3	3.499	3.18
Acetylene	0.75	0.11	0.65	0.11	6	1.285	" "	6	1.285	2.44
Methane	5.70	0.28	5.40	0.16	6	1.860	" "	5	1.860	2.57
Ethane	0.58	0.04	0.60	0.07	6	0.496	" "	5	0.496	2.57
Benz./Tol.	0.90	0.12	0.98	0.04	6	1.264	" "	4	1.264	2.78

* Statistical Criteria: Taken at 95% confidece interval and for two cases.
First case - assumes the two "population" variances are equal.
Second case - assumes the two "population" variances are not equal.

are 79.8 and 79.6 percent by mass using nitrogen and sand thermofor respectively. The ethylene yield was 6.1 percent in both cases. Two statistical T tests (summarized in Table 28) also confirm that at the 95% confidence level no difference in total gas or component yields is apparent, with the exception of propylene. One test assumes that the two "population" variances (i.e. one for the nitrogen thermofor pyrolysis and the other for sand thermofor pyrolysis) are equal, while the other assumes that the population variances are not equal. The outcomes were similar for both tests. Therefore, preliminary tests would suggest that no difference exists when comparing the use of the two types of thermofor pyrolysis of cellulose at 800°C. A more comprehensive study using other temperatures and residence times should be conducted in order to confirm whether this conclusion can be generalized.

10.7 Water-Gas Shift Reaction Study

The literature review presented earlier in this report suggested that the water-gas shift reaction might play some role in determining the final product distribution of the fast pyrolysis gases. This reaction is represented as follows:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

It was decided to conduct a limited number of experiments in the Ultrapyrolysis system, and to monitor the extent of the homogeneous reaction on a time scale comparable to that for the fast pyrolysis of biomass. Carbon dioxide and hydrogen were selected as the feedstock gases due to their convenience with respect to procurement, feeding and metering (i.e. the reverse reaction would require steam generation and flow metering). A mixture consisting of 82.45 molar % hydrogen and 17.55 molar % carbon dioxide was procured from Matheson in Whitby Ontario. The experimental procedure was similar to that reported for biomass experiments with the exception that feedstock gas flow was controlled and measured with rotameters. Feedstock gases were injected through the biomass injection tube where they were rapidly heated to the reaction temperature by the inert nitrogen thermofor. The resulting mixture was diluted such that the nitrogen accounted for about 80% (by volume) of the total reacting gas. Experiments were conducted at 850 and 900°C.

The results of the water-gas shift reaction, investigated in the Ultrapyrolysis system, are given in Table 29. The initial hydrogen and carbon dioxide concentrations (i.e. the concentrations at $t = 0$) are tabulated along with the concentration of CO_2 and CO at the indicated residence times. Equilibrium concentrations of CO_2 and CO, accounting for the reactor conditions of pressure, temperature and initial concentrations, are also tabulated. The predicted concentration of CO_2 for each experiment is based on a homogeneous kinetic model for the forward direction of the reaction (i.e. $CO_2 + H_2 \rightleftharpoons CO + H_2O$) as reported by Kochubei and Moin [176]. The reaction has been treated as an irreversible process since a modest literature review failed to provide the homogeneous kinetics of the reverse reaction (heterogeneous reaction kinetic studies were abundant). However, the treatment of this reaction as irreversible proved to be adequate since the analysis of the homogeneous model revealed that the kinetics were apparently much too slow to be a factor in the context of fast pyrolysis (i.e. if

TABLE 29. WATER-GAS SHIFT REACTION EXPERIMENTS AT 850 AND 900 C: DATA SUMMARY

RUN NO.	TEMPERATURE (C)	RESIDENCE TIME (ms)	COMPONENT CONCENTRATION (molar * E4)*							APPROACH TO EQUILIBRIUM
			$[H_2]_o$	$[CO_2]_o$	$[CO_2]_t$	$[CO_2]_e$	$[CO_2]_p$	$[CO]_t$	$[CO]_e$	$[CO]_t/[CO]_e$
WG2	850	178	19.2	3.93	3.61	0.65	3.93	0.43	3.40	0.13
WG3		342	25.9	5.31	4.52	0.87	5.31	0.94	4.59	0.20
WG4		91	29.4	6.02	5.75	0.99	6.02	0.42	5.18	0.08
WG12		434	31.4	6.44	4.45	1.06	6.44	1.58	5.55	0.28
WG5	900	98	26.0	5.34	4.79	0.78	5.34	0.68	4.69	0.14
WG6		191	20.6	4.21	3.67	0.62	4.21	0.64	3.72	0.17
WG7		350	26.7	5.47	4.19	0.80	5.47	1.44	4.81	0.30

* Initial concentrations of CO and H_2O are zero. The concentrations of H_2O at time "t" and at equilibrium are equal to the concentrations of CO at time "t" and at equilibrium, respectively. The concentration of H_2 at time "t" is equal to the initial concentration of H_2 minus the quantity $[CO_2]_o - [CO_2]_t$.

SUBSCRIPTS:	o	initial concentration
	t	concentration measured at residence time "t" ms
	e	theoretical equilibrium concentration
	p	concentration predicted by theoretiacl kinetic model (assumes homogeneous irreversible kinetics)

treated as reversible, the net forward rate would be even slower than the irreversible forward rate). The results of this kinetic analysis are summarized as the predicted CO_2 concentrations in Table 29, and a sample of the results of the computer analysis is given for two experiments in Appendix 14.7.

It is obvious that the actual experimental data does not agree with the results predicted by the kinetic model. The approach to equilibrium was measured by taking the ratio of the actual CO concentration to that expected at equilibrium (Table 29). The results which are plotted as a function of residence time in Figure 42, indicate that while equilibrium has not been reached, the reaction has proceeded to a significant extent over the fast pyrolysis time scale. The kinetic model predicts that the reaction will not occur to any significant extent (for example, a 5% reduction in initial CO_2 concentration) until after 25 seconds at 900°C, and after 100 seconds at 850°C (Appendix 14.7).

The disagreement in the data can perhaps be resolved in terms of an unfortunate oversight in the operating procedure. The water-gas shift experiments were conducted after the cellulose pyrolysis series was completed and before the systematic wood pyrolysis experiments were initiated. However, several preliminary trials with wood were carried out prior to the water-gas shift study in order to gain experience with the new feedstocks and to note qualitative differences from the cellulose trials (i.e. differences in liquid and char yields which must be handled by the downstream recovery units). Since these

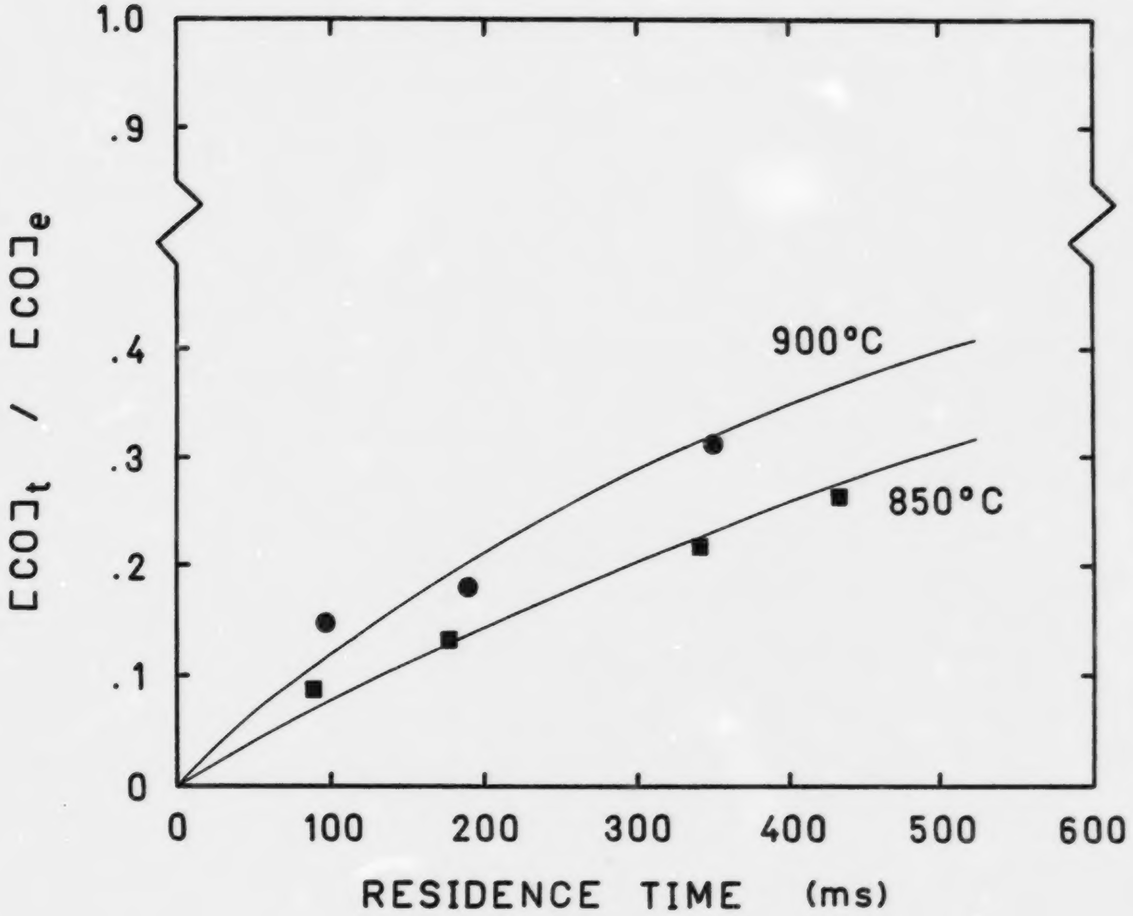


Figure 42. Water/Gas Shift Reaction Approach to Equilibrium: $[CO]_t$ / $[CO]_e$ vs Residence Time

wood experiments were of a preliminary nature, the reactor system was not routinely inspected (as was the case for cellulose experiments, until it was obvious that no char accumulation was occuring).

The water-gas shift trials were initiated after these preliminary wood experiments, and the reactor system was not inspected for char/ash accumulation. Upon completion of the water-gas study, the reactor system was inspected and a 3 cm plug of char/ash was found in the tubular reactor. Smaller plugs were also found, and it was very likely that surface catalysis was occuring in the "porous bed reactor". Therefore, the reaction could not be described by a homogeneous kinetic model. This explanation may be further substantiated by the data represented in the Figures appearing in Appendices 14.4 to 14.6, which illustrate that the yields of CO, H_2 and CO_2 remain relatively constant at non-equilibrium concentrations in the asymptotic region during the fast pyrolysis of biomass (even at high temperatures).

The water-gas shift study did not accomplish its intended objective which was to monitor the homogeneous reaction. The published kinetic model and actual results from the fast pyrolysis of cellulose and wood, suggest that homogeneous water-gas shift reaction kinetics are much too slow to allow this reaction to play a significant role during fast pyrolysis. It was hoped that an independent study in the Ultrapyrolysis system would confirm this. The study did suggest that the heterogeneous (catalyzed) reaction is significant on a fast pyrolysis time scale.

10.8 Fast Pyrolysis Kinetics

The objective of the kinetic study of fast pyrolysis was to generate an empirical kinetic model as opposed to a theoretical mechanistic model. As reflected in the kinetic literature which was referenced previously in the literature review (Chapter 4.0), it is extremely difficult to evaluate the detailed mechanism of biomass fast pyrolysis without sophisticated analytical equipment due to the complexity and number of the primary products. On the other hand, an empirical kinetic model is much more tractable. It is useful in engineering applications as a predictive tool to optimize yields of desirable products, and also to assist in reactor design. This latter method was therefore adopted to provide an adequate model for the rate of appearance of the principal gaseous products from cellulose and wood.

A simple and convenient approach to kinetic modeling assumes that the solid biomass decomposes directly to each individual gas component by a single independent pathway and that the kinetics of the decomposition can be represented by a unimolecular first-order reaction. This approach has been widely used in representing the kinetics of the thermal decomposition of many solid feedstocks [25,108]. The following rate equation is thereby derived:

$$V = V^* (1 - e^{-kt})$$

where V represents the yield (expressed as a % by mass of the dry feedstock) of a component at residence time "t" and temperature "T",

TABLE 30. FAST PYROLYSIS OF CELLULOSE: SUMMARY OF KINETIC PARAMETERS V* AND k

COMPONENT	PARAMETER	REACTION TEMPERATURE (C)							
		650	700	750	800	825	850	875	900
Total Gas	V*	27.6	50.6	69.3	80.1	81.0	83.5	85.1	87.7
	k	3.85	5.15	9.12	13.4	17.3	21.5	34.5	42.1
Hydrogen	V*	-	0.9	1.3	1.7	1.7	1.7	1.8	1.9
	k	-	2.16	5.63	8.28	9.77	17.0	14.0	14.5
Carbon Monoxide	V*	20.9	37.3	50.6	57.4	58.2	59.8	60.7	62.6
	k	3.63	5.32	9.25	14.1	17.8	21.7	35.8	43.9
Carbon Dioxide	V*	2.3	3.6	5.2	5.7	5.7	5.7	5.8	6.0
	k	10.6	9.23	7.49	12.6	18.2	24.9	41.4	44.1
Ethylene	V*	1.3	3.2	5.1	6.1	6.5	6.9	7.1	7.3
	k	4.28	4.32	7.50	14.0	16.4	20.1	32.0	39.5
Methane	V*	1.2	3.5	4.6	5.9	6.0	6.2	6.4	6.5
	k	1.88	1.82	4.73	7.02	7.47	10.1	13.9	18.7
Acetylene	V*	-	0.3	0.7	1.1	1.1	1.4	1.7	1.9
	k	-	14.8	11.1	16.3	27.3	32.8	42.4	44.1

TABLE 31. FAST PYROLYSIS OF IEA POPLAR: SUMMARY OF KINETIC PARAMETERS V* AND k

COMPONENT	PARAMETER	REACTION TEMPERATURE (C)				
		700	750	800	825	850
Total Gas	V*	38.5	57.0	65.4	73.0	73.2
	k	10.2	11.3	17.5	19.0	31.8
Hydrogen	V*	0.3	0.7	0.9	0.9	1.0
	k	2.46	5.08	7.09	13.6	12.1
Carbon Monoxide	V*	24.1	34.6	39.9	42.7	43.7
	k	8.36	10.9	18.2	19.6	30.1
Carbon Dioxide	V*	7.4	9.8	10.2	12.4	11.7
	k	29.6	17.9	17.0	22.7	49.6
Ethylene	V*	2.0	3.3	4.2	4.8	5.0
	k	6.39	7.76	13.4	13.6	21.6
Methane	V*	2.6	4.6	5.5	6.4	6.5
	k	6.54	6.59	9.75	12.0	16.8
Acetylene	V*	0.2	0.4	0.7	0.8	0.9
	k	4.69	8.25	12.6	14.5	20.2

The kinetic model is first-order and of the following form:

$$V = V^* [1 - \exp(-kt)]$$

V = mass yield (% by mass) of component at temperature "T" and time "t" (s).
V* = asymptotic (maximum) yield (% by mass) of component at temperature "T"
k = Arrhenius rate constant (s-1) at temperature "T"
t = reactor residence time (s)

V* is the maximum attainable (i.e. asymptotic) yield (% by mass) of the particular product at temperature "T", and k is the Arrhenius rate constant. The Arrhenius expression is given by:

$$k = k_0 \; e^{-E_a/RT} \tag{2}$$

where k is the rate constant, k_0 is the frequency factor or pre-exponential constant, E_a is the apparent activation energy of the reaction, R is the universal gas constant, and T is the absolute reaction temperature. Best fit values for the kinetic parameters (V* and k) were estimated for the total gas and all principal gaseous products using a least squares non-linear regression procedure. These parameters are summarized in Tables 30 and 31 for a cellulose and poplar experiments, respectively.

The solid lines which represent the total gas yields from cellulose in Figures 11 to 18, and the individual gas product yields in Appendix 14.4, are the result of the modeling procedure (i.e. the best fit of the kinetic parameters V* and k). Corresponding results for the yields from IEA poplar are shown as the solid lines in Figures 19 to 23 and Appendix 14.5. A good fit of the data to the first-order model is apparent for most gases over the entire temperature range. The exceptions are the yields of carbon monoxide and carbon dioxide from cellulose and poplar at the lowest pyrolysis temperatures that were investigated (i.e. 650 and 700 °C), and the yield of methane from poplar at 700°C. A comparison of the experimental data (for these products which deviate moderately from first-order behaviour) to the solid curves, illustrates that the actual yields do not appear to pass through the origin when the residence time approaches zero.

That is, the yields of those products which do not closely follow the model are positive when extrapolated back to zero residence time "t_0". The model requires that the curve pass through the origin, and the result is a moderate deviation of actual data from first-order behaviour for some products at the lower pyrolysis temperatures.

Since some product yields do not appear to pass through the origin at lower temperatures, one might be tempted to suggest one of the following preliminary explanations:

1. There are physical transport limitations (such as heat or mass transfer) to the pyrolysis process in the Ultrapyrolysis equipment.
2. There is some latent period of activation associated with biomass fast pyrolysis.
3. The estimates of reactor residence times are in error.

However, if there were physical limitations or latency, none of the product yields would be expected to pass through the origin at t_0, and the yields would remain at zero until some positive residence time "t". In fact, all product yields do appear to pass through the origin with the exception of CO and CO_2 for cellulose trials. In addition, as stated previously, those product yields which do not pass through the origin have positive values at t_0.

With respect to errors associated with estimates of the residence time, this is unlikely since the reactor volume has been accurately determined (by independent methods), and the injector Reynold's numbers coupled with the basic tubular reactor design would suggest that ideal plug-flow behaviour is approached. The experimental results of the ethane cracking study were compared to literature kinetics (Section 10.5) and also testified of the integrity of the estimates of reactor residence time and temperature.

A more suitable explanation of the occasional deviations from first-order behaviour (i.e. positive yields of some products at t_0) involves the concepts of "prompt gas" and "instantaneous" volatilization of the solid biomass feedstock. The term "prompt gas" was coined by Diebold [177] in order to distinguish between those non-condensible gases produced during the primary biomass depolymerization step from those produced later during the decomposition of the primary vapours. Applying this concept to the Ultrapyrolysis data, one can extrapolate the experimental yield data for the relevant product gases back to zero residence time (t_0) in order to estimate prompt gas yields. From Figure 11 and Appendix 14.4.1, the prompt yields of total gas, carbon dioxide and carbon monoxide from cellulose are estimated to be 8.0, 6.0 and 1.5 percent by mass, respectively. The prompt yields of total gas, carbon dioxide, carbon monoxide and methane from poplar (Figure 19; Appendices 14.5.1 and 14.5.6) are 7.0, 5.0, 1.0 and 0.5 percent by mass, respectively. These estimates are in excellent agreement with those reported explicitly by Diebold [177] and implicitly by Scott (Section 10.4). The magnitude of the values of the prompt gas yields gives an indication as to why the deviation from first-order behaviour is so significant at lower temperatures (where the estimated prompt value is a large fraction of the total value) and negligible at the highest temperatures (where the amount of secondary gas dominates the prompt gas).

The fact that the non-gaseous products are liquid rather than solid char or unpyrolyzed feedstock for cellulose pyrolysis (even at extremely short residence times) would seem to suggest that the solid phase decomposition to primary liquids is practically instantaneous in the Ultrapyrolysis reactor system (i.e. the time for primary depolymerization to occur is a negligible fraction of the time scale for the cracking of primary vapours to condensible gases). This is likely a result of a combination of the inherently high heat transfer rates and the small cellulose particle size. Therefore, the kinetic model is best described as representing the rate of appearance of the gas and its components from the primary pyrolytic liquids (vapours). The prompt gas would therefore appear at "t_0" in the kinetic model. Subtraction of the estimates of prompt gas yields from the totals of the actual gas yields should give a better fit of the data to the first-order model, especially at lower residence times where "prompt yields" comprise an ever-increasing fraction of the actual gas yields. Insufficient time was available to fit the adjusted data to the first-order model.

An estimation of the apparent activation energy (E_a) associated with the fast pyrolysis of biomass to produce total gas and individual gaseous components can be accomplished using the Arrhenius equation. A plot of ln(k) vs 1/T should give a straight line with a slope of $-E_a/R$ and an intercept representing the frequency factor k_0. The Arrhenius plot for total gas production from cellulose is given in

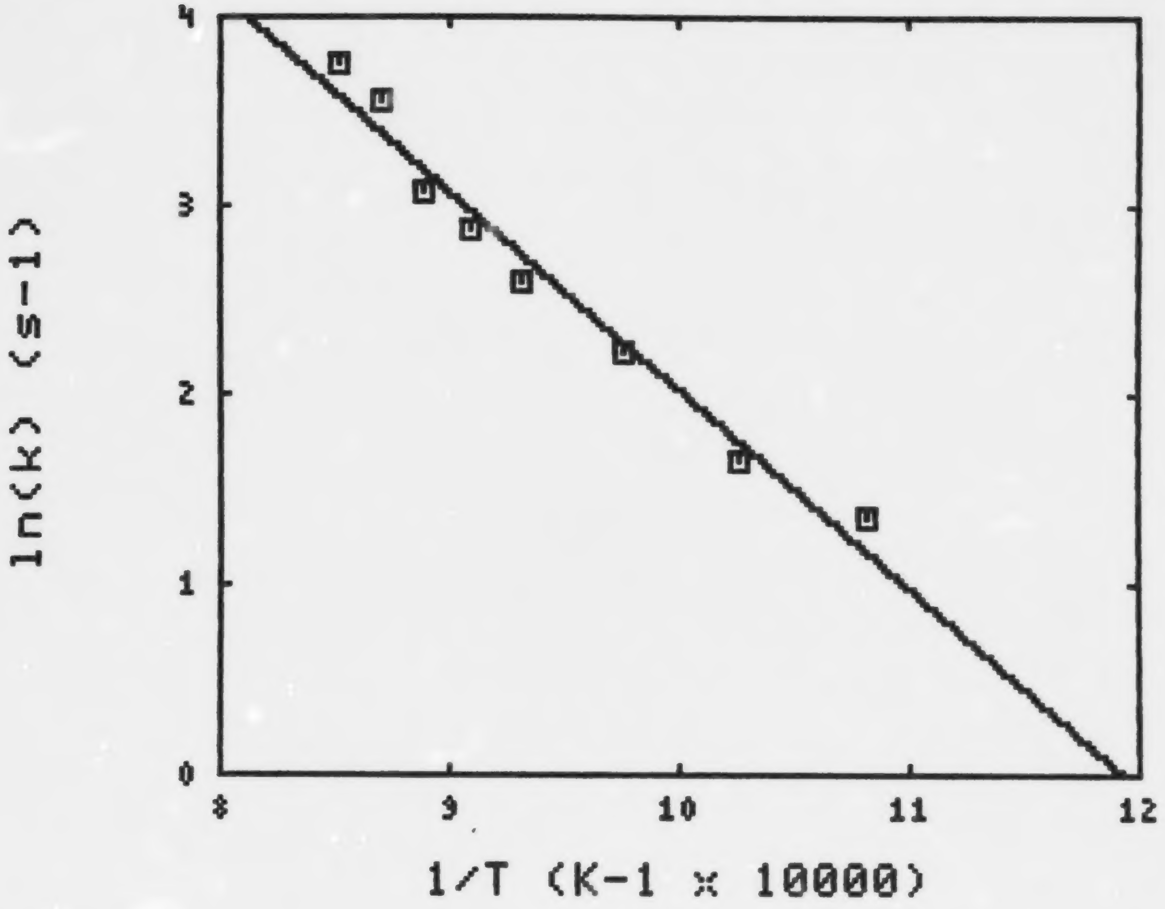


FIGURE 43. Arrhenius Plot for Total Gas Production from Cellulose

Figure 43. Corresponding plots for the individual gas products from cellulose are given in Appendices 14.8. As stated previously, the data used to generate these curves includes the prompt gas. The latter should be subtracted from the totals prior to modeling. Therefore, there is a significant "curve" away from the expected straight line as evidenced in the CO and CO_2 plots. This phenomenon is most significantly illustrated in the CO_2 plot (Appendix 14.8) for cellulose pyrolysis where the prompt CO_2 comprises practically all of the total CO_2 at 650°C. If these were removed, the estimate of the rate constant at 650°C would be drastically reduced and the plot would "bend" back towards a straight line fit with the higher temperature data. Since this effect is minimal at high temperatures where the prompt gas represents a relatively small fraction of the total, the net result would be a higher estimate of the value of the apparent activation energy, and a better fit of the Arrhenius plot. The deviation from the straight line at high temperatures on the Arrhenius curve for hydrogen (Appendix 14.8) might suggest that the water-gas shift reaction is in fact beginning to compete with the thermal decomposition reactions.

Using the SI value of the universal gas constant (i.e. 8.3144 J K^{-1} mol^{-1}), the estimated apparent activation energies with their associated standard errors of the estimate are given for cellulose in Table 32. It is important to reiterate that the estimates of apparent activation energies for the production of total gas, CO and CO_2 will increase moderately when the prompt gas is adequately dealt with in the kinetic model. In addition, the standard errors of the estimates will also be reduced accordingly. Nevertheless, for discussion purposes, the tabulated E_a estimates are above the range transport-controlled kinetics and in the lower range of chemical kinetic control. These values are typical of a complex chemical pathway which is represented by a simple reaction model. Better estimates of the apparent activation energies will be made using adjusted data (i.e. accounting for the prompt gas), and will be reported in future publications.

TABLE 32. APPARENT ACTIVATION ENERGIES AND FREQUENCY FACTORS ASSOCIATED WITH THE FAST PYROLYSIS OF CELLULOSE (650 to 900 C)

KINETIC CONSTANTS*	GAS PRODUCT						
	Gas	H_2	CO	CO_2	C_2H_4	C_2H_2	CH_4
Apparent Ea (kJ/mol)	86.9	92.3	89.4	57.9	85.2	99.9	86.5
Standard Error	6.1	12.3	5.6	14.6	8.3	9.6	7.9
ln (ko) (s-1)	12.5	12.4	12.8	9.4	12.2	14.1	11.6
Standard Error	0.7	1.4	0.6	1.6	0.9	1.0	0.9
ko (s-1 * E5)	2.64	2.41	3.56	0.12	2.04	13.3	1.13

* As discussed in the text, these estimates of the kinetic constants are based on the data which includes the "prompt gas". Analysis of the refined data (i.e. with the prompt gas removed) will give higher estimates of apparent activation energies for CO, CO_2 and Total Gas (also corresponding lower standard errors). The most significant increase will occur in the estimated activated energy for CO_2 production.

Ea - activation energy
Ko - frequency factor (pre-exponential constant)

11.0 CONCLUSIONS

The following general conclusions are drawn from the previous discussion:

1. The gas-phase kinetics for the production of the principal fast pyrolysis product gases from cellulose were systematically characterized and found to fit a first-order model quite well. It is believed that this is the first time that such a characterization has been accomplished under isothermal fast pyrolysis conditions.

2. Fast pyrolysis consists primarily of biomass depolymerization and primary vapour thermal decomposition. There is little evidence of significant gas reactions such as the cracking of light hydrocarbons and the water-gas shift reaction.

3. The Ultrapyrolysis equipment appears to be a reliable tool for studying fast kinetics. Experimental data for ethane cracking agreed quite well with the yields predicted by generally-accepted kinetic models. Therefore, published models for other gas-phase reactions could presumably be coupled with the empirical cellulose kinetic model to give a more comprehensive model to predict product distributions at longer residence times.

4. Maximum yields of ethylene, total unsaturates and total hydrocarbons from cellulose were 7.3, 10.3 and 17.5 percent (by mass) respectively at 900°C. These yields are still increasing with temperature at 900°C (the highest temperature investigated) but not at such a significant rate as was the case at lower temperatures.

5. Methane does not appear to act synergistically with biomass to enhance ethylene yields.

6. Comparison of Ultrapyrolysis data in the range of 650 to 900°C overlaps quite nicely with fluidized bed fast pyrolysis data (Waterloo University) conducted over a lower temperature range, giving congruent results from 400 to 900°C.

7. Total liquid yields (i.e. condensibles) are quite high, approaching 90 percent (by mass), at the lower temperatures and residence times (i.e. less than 100 ms at 650°C). Characterization of these liquids should provide mechanistic insights with respect to the primary pyrolysis pathway.

8. Although sand thermofor is expected to greatly enhance the heat transfer to larger biomass particles (allowing a correspondingly high heating rate), no difference between sand and gaseous nitrogen heat carriers was detected with respect to effects on the product distribution using finely powdered feedstocks. This allows nitrogen to be used to determine general chemical kinetics.

while heat transfer effects associated with sand (and subsequent commercial-scale reactor operation using larger feedstock particles) can be incorporated when required for predictive reactor modeling.

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14.0 APPENDICES

14.1 Ultrapyrolysis Publications

The following list represents only that portion of Ultrapyrolysis papers which were published during the current research program (i.e. funded by NRC).

1.* Graham, R.G., B.A. Freel, M.A. Bergougnou and L.K. Mok. 1986. "The Kinetics of the Fast Pyrolysis of Cellulose at 900°C". Proceedings of the Conference on Energy from Biomass and Wastes X. Washington, D.C. April 7-10, 1986. Institute of Gas Technology. Chicago, IL (In Press).

2.† Graham, R.G., B.1A. Freel, R.P. Overend, L.K. Mok and M.A. Bergougnou. 1986. "The Ultra-Rapid Fluidized (URF) Reactor: Application to Determine the Kinetics of Fast Pyrolysis Ultra-Pyrolysis of Cellulose". Proceedings of the 5th Engineering Foundations Conference on Fluidization. Helsinger. Denmark. May 18-23, 1986. (In Press).

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5.† Mok, L.K., R.G. Graham, B.A. Freel, M.A. Bergougnou and R.P. Overend, 1985. "Fast Pyrolysis (ULTRAPYROLYSIS) of Cellulose and Wood Components". Journal of Analytical and Applied Pyrolysis 8: 391-400.

6.† Graham, R.G., M.A. Bergougnou, L.K. Mok and H.I. de Lasa. 1985. "Fast Pyrolysis (ULTRAPYROLYSIS) of Biomass Using Solid Heat Carriers". In Fundamentals of Thermochemical Biomass Conversion. R.P. Overend et al. (Editors). Elsevier Applied Science Publishers Ltd. New York. pp. 397-410.

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10.* Mok, L.K., R.G. Graham, R.P. Overend, B.A. Freel and M.A. Bergougnou. 1984. "ULTRAPYROLYSIS: The Continuous Fast Pyrolysis of Biomass". Proceedings of the Bio-Energy '84 World Conference. Gothenburg, Sweden. June 18-21, 1984. The Bio-Energy Council. Washington, D.C.

11. Graham, R.G., M.A. Bergougnou, L.K. Mok, H.I. de Lasa and B.A. Freel. 1984. "ULTRAPYROLYSIS of Cellulose and Wood Components". Proceedings of the Fifth Bioenergy R&D Seminar. S. Hasnain (Editor). Elsevier Science Publishers Ltd. London, pp. 386-390.

12.* Graham, R.G., M.A. Bergougnou, L.K. Mok, B.A. Freel and H.I. de Lasa. 1984. "Continuous Fast Pyrolysis of Biomass Using Solid Heat Carriers". Proceedings of the Conference on Energy from Biomass and Wastes VIII. Lake Buena Vista, FL. January 30 to February 4, 1984. Institute of Gas Technology. Chicago, IL. pp. 1417-1433.

13.† Mok, L.K., R.G. Graham, H.I. de Lasa, B.A. Freel and M.A. Bergougnou. 1984. "Application of Ultra-Fast Fluidization to the Fast Pyrolysis of Cellulose (ULTRAPYROLYSIS)". American Institute of Chemical Engineers Symposium Series 234. Volume 80: 70-79.

14.* Meunier, M., R. Sumner, S.L.K. Mok and R.G. Graham. 1984. "Ultra-Rapid Fluidization (URF), A New Reactor Concept: Application to Pyrolysis of Wood Components and to Other Industrial Processes". Proceedings of the VIIth All-Union Heat and Mass Transfer Conference. Minsk, USSR. May 21-23, 1984. Institute of Mass Transfer. Minsk, USSR.

†Fully refereed
*Partly refereed (extended abstract)

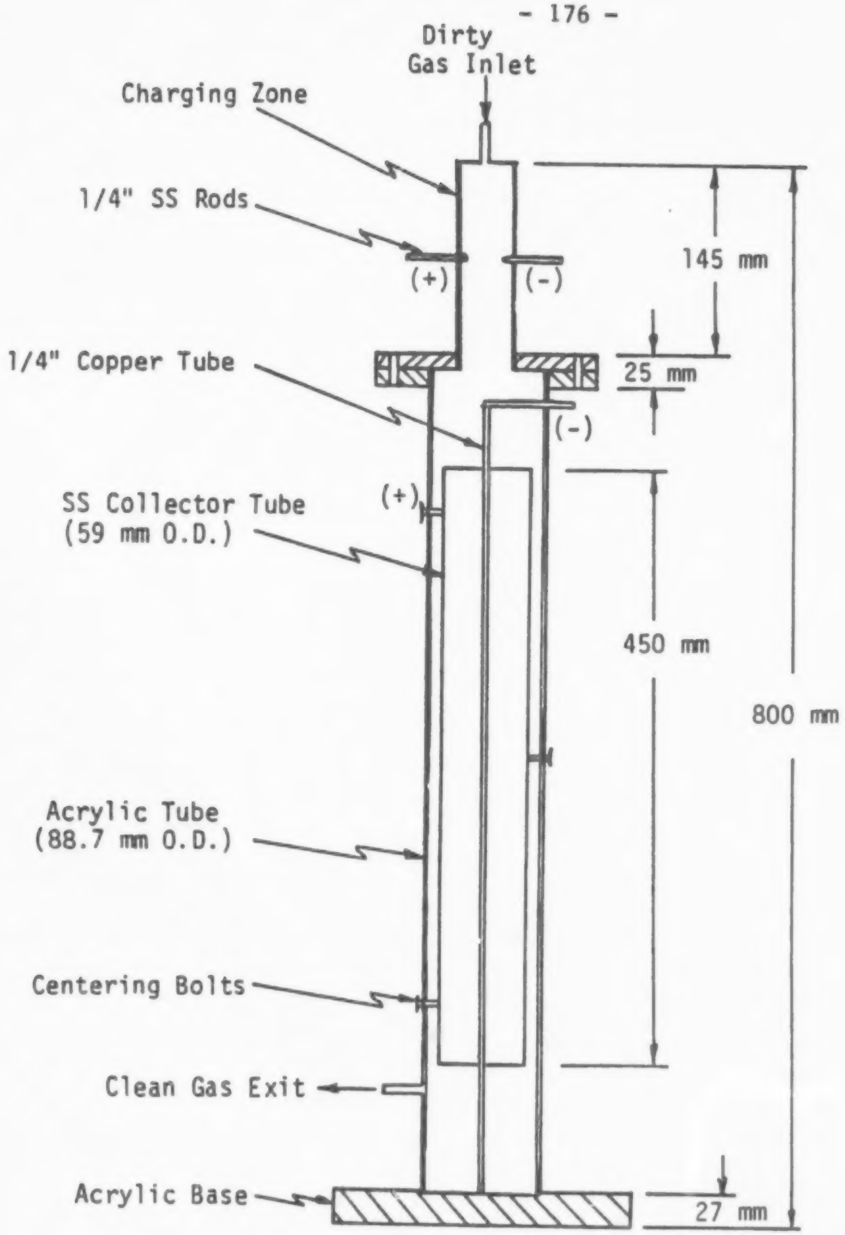
14.2 Detailed Design of Principal New Components

14.2.1 Electrostatic Precipitator Design

Initial Ultrapyrolysis experience with biomass at lower temperatures (<800°C) and/or residence times (<100 ms), indicated that a more efficient collection system would be required to handle the increasing "condensible" and char yields. Originally the collection train consisted of a coil condenser and an SS (stainless steel) porous filter (0.5 μm pore size). However, as the amount of material fed into the system was increased (to improve mass balancing) and also as the yields of condensibles and chars went up, the capacity of the collection system was exceeded resulting in pressure increases and subsequent system upset.

The high efficiency filter (SS sintered filter; 2-3/4" dia. by 36" long) was capable of removing particles as small as 0.5 μm. However, the surface area allowed for a collection of only 6-10 g of material before undesirable pressure increases were observed. Experiments which were conducted at low residence times and temperatures produced high yields (>60%) of organic liquids which saturated the filter after only 15-25 g of carbonaceous feedstock had been fed. To alleviate this problem, an electrostatic precipitator (EP) was considered to remove the majority of organic liquid vapours prior to the filter.

Commercial EP's applicable for use in the UP system, were found to



Cross-Section

Scale 1 mm =.5 cm

Figure 14.2.1. Plexiglass/ABS Electrostatic Precipitator Design

be very expensive (i.e. $10,000; Westinghouse, London). For this reason it was decided to design and build a laboratory model. After several "quick and dirty" tests using various configurations and power sources, a two stage electrostatic precipitator was designed and built (Figure 14.2.1). Due to the fragile nature of the plexiglass EP, a similar design was constructed of ABS tubing.

Although testing and subsequent cellulose kinetics experiments indicated stable operation, good efficiency and negligible pressure drop, the unit had several shortcomings:

1. Due to the material of construction (plexiglass, ABS body), solvent extraction of the pyrolytic organic liquid deposited in the unit was not possible. After several experiments it was found that the methanol used for liquids recovery was dissolving the plexiglass and ABS bodies.
2. Since the collector tube and repelling tube were permanently fixed in the bottom section of the precipitator, cleaning of these parts was difficult.
3. Varying the gap of the charging zone rod and needle was not possible as they were fixed in the upper zone body. This resulted in a lower potential available for charging.
4. The electrical properties of the plexiglass body are such that shock hazards existed if personnel made any attempts to adjust any piece of equipment near the precipitator.
5. Shorting between the repelling rod and the collector cylinder occurred as a result of pyrolytic liquid accumulating in the precipitator.

As a result of these considerations, a new precipitator was designed, built and tested. The design was based on a migration velocity calculation for an average particle size. This precipitator, unlike the previous design, was constructed of TEFLON to allow for complete solvent extraction of liquid organic materials deposited in the EP. In addition, the electrical properties (i.e. electrical resistivity) are much more suitable than for many other plastics, thereby reducing the chances of electrical shock and shorting. The collector cylinder can be readily removed for ease of cleaning along with any other component of the EP. A variable 0 to 60 KV (D.C.) power supply was procured from the Electrical Engineering Group (U.W.O.) in order to provide the required electrical field (i.e. potential difference) in both the charging section and the collection zone of the EP.

The negative lead is connected to the "needle" electrode and the positive is connected to the "rod" electrode in the charging section. Gyrolok fittings used in the charging zone allows for adjustment of the electrode gap. This general arrangement produces a negative corona condition which allows for higher allowable potential differences (i.e. as opposed to a positive corona). The maximum potential difference is the voltage at which "sparkover" (i.e. arcing between electrodes) begins to occur.

Thorough safety considerations are essential when using an EP. The power supply is safe-guarded internally and will automatically shut down if the current exceeds a pre-set value. Thus, direct contact by the operator with an electrode will result in an immediate power cut-off. The total power could deliver a powerful jolt but would not cause direct serious injury. A switch has been installed on the main control panel which must be actuated before the power supply can be turned on. Two operators are therefore required to activate the EP unit. The precipitator leads and electrodes have been shielded with vinyl tubing to preclude direct operator contact.

The operating procedure is summarized as follows:

1. The unit is not activated until the experiment is about to commence. The EP operator then signals the main operator to actuate the control panel switch.
2. The power level is initially set at a low voltage between 6 and 15 kV.
3. When the pyrolytic "smoke" is observed entering the unit, the voltage is increased to its maximum level (i.e. where sparkover commences in the charging zone).
4. Subsequent voltage adjustment may be required in response to vapour flow fluctuations in order to maintain maximum removal efficiency.
5. Upon completion of the run, the EP operator signals the main operator and both power switches are shut off.

14.2.2 Cyclonic Condenser Design

A conventional cyclone design was used as the basis for the cyclonic condenser/separator design. The gas/vapour stream enters the cyclonic vessel through a tangential inlet at a high velocity, thereby allowing a centrifugal force to develop. This force drives the stream towards the wall where good heat transfer is achieved (i.e. heat removal from the gases). The condensible vapours are more dense than the permanent gases and condense due to their intimate contact with the wall. Gravity takes these liquids downwards to a collection vessel at the base of the vessel while the gas stream reverses direction and passes upwards through the annulus and out the top of the cyclone. This "clean" exit gas can also serve to remove additional heat from the inlet stream. In summary, the cyclone acts as an enhanced settling chamber for organic condensibles by increasing the stream density through an applied centrifugal force.

In the Ultrapyrolysis system, the product/thermofor mass flowrates (i.e. the stream exiting from the fast cooler) vary from 20 to 100 g/min. A median value of 35 g/min was used in the cyclone design, and the cyclone inlet velocity was taken to be 25 m/s. Cyclone dimensions were selected to ensure adequate heat transfer area for product stream cooling (to approximately room temperature). These dimensions are indicated on the schematic diagram (Figure 14.2.2).

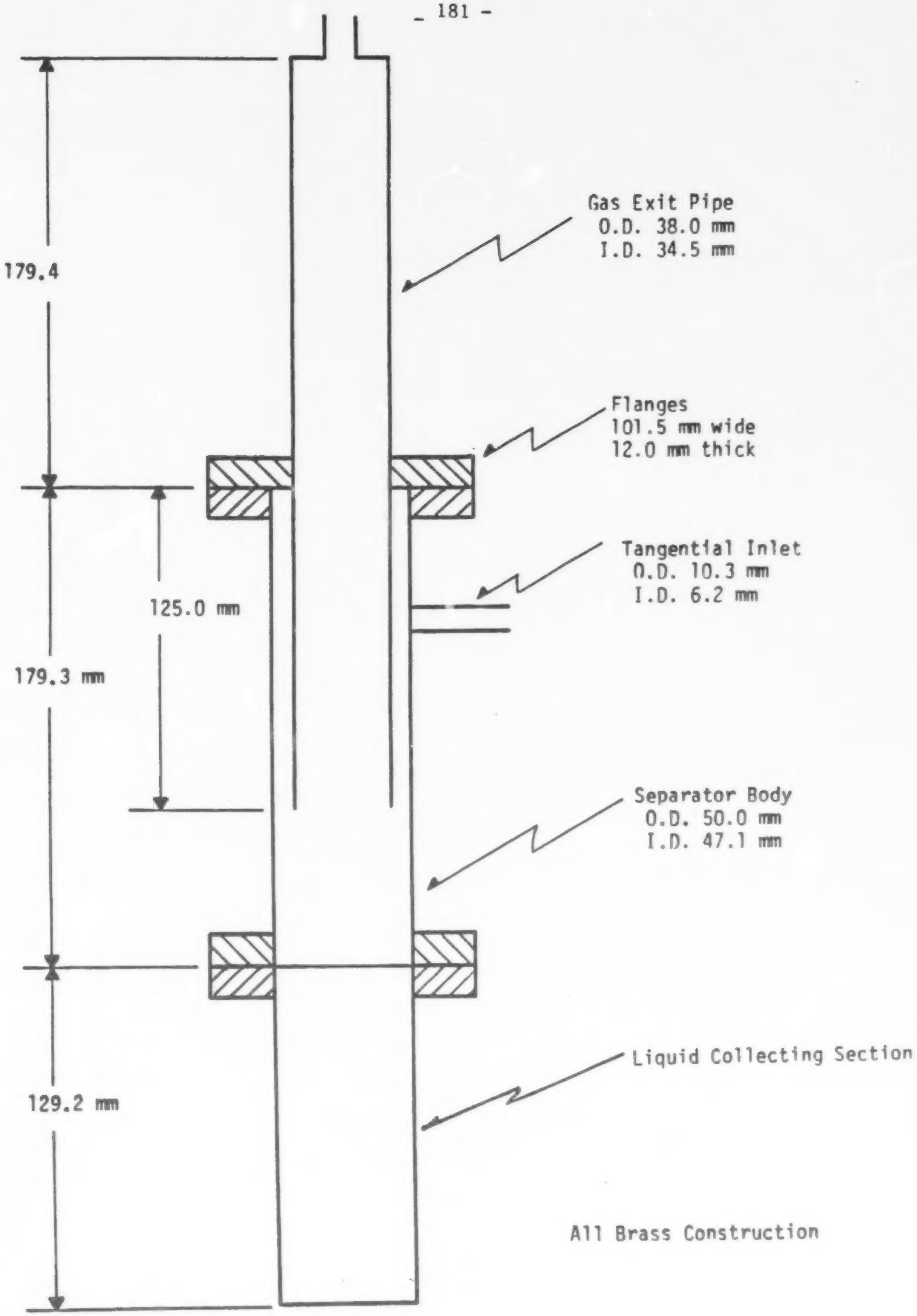


Figure 14.2.2 Cyclone Condenser Schematic

14.3 Sample Data Sheets and Computer Printouts for a Selected Cellulose Pyrolysis Experiment (CK 314)

General Data Sheet

Residence Time Summary

Gas Product Summary

Mass Balance Data Sheet

UP DATA SHEET: Run # CK-314 Date: 13/8/85 No. Inserts: 12

TEMPERATURES:

Ambient temp.	22	C	Coil Oven (top)	1100	C
Nitrogen	21.5	C	Coil Oven (bot)	1100	C
Reactor Oven (top)	862	C	Injector (M.I.)	83	V
Reactor Oven (bot)	860	C	Thermovort. Oven	870	C
Thermofor Line (1)	880	C	Reactor Wall (7)	850	C
Thermofor Line (2)	870	C	Cryovortactor (8)	370	C
Injector Oven (3)	960	C	Heat Exchang. (9)	-	C
Thermovortactor (4)	850	C			
Reactor Cavity (5)	850	C	Preheater-T (11)	1020	C
Reactor Wall (6)	852	C	Preheater-B (12)	-	C

PRESSURES:

Ambient Pressure 764 mmHg

Time (m/s)	0	5	10			$\bar{x}$
Biom. Feeder (psig)						
Therm. Feeder (psig)	1.6	2	2.1			2
Cryo. Exit (psig)	1.4	1.7	1.9			1.8

ROTAMETER DATA:

Time (m/~~s~~)	2		5		8				
	psig	scale	psig	scale	psig	scale	psig	scale	
Cryo.Ext.N2	1.4	110	1.8	110	1.9	110	2.0	110	1.8,110
Thermofor	-	-	-	-	-	-	-	-	
Biomass	1.6	45	2		2.1				2,45
B/T Ext.N2	6.4	80	7	80	7	80			7,80

BIOMASS FLOW:

Motor Setting	18	%	Calib. Flowrate	~2	g/min
Biomass Fed	24.0	g	Initial Time	6	s
Biom. Bypassed	0.7	g	Final Time	10' 6	s
Biom. Pyrolyzed	23.3	g	Time of Pyrolysis	10'	~~s~~

Biomass Flowrate 2.33 g/min

THERMOFOR FLOW:

Motor Setting	-	%	Calib. Flowrate	-	g/min
Time Interval	-	s			

BAG PRESSURES:

	Bag 1	Bag 2	Bag 3	Bag 4
Initial P (mmHg)	730	411	693	-
Final P (mmHg)	411	95	365	
Delta P (mmHg)	319	316	328	
Tank Temp. (C)	24	25	26.5	

COMMENTS: ______________________________

RGG
Initials

```
     ULTRAPYROLYSIS REACTOR RESIDENCE TIME PROGRAM
     *********************************************


EXPERIMENTAL RUN: CK-314      DATE: AUG.13/85

EXPERIMENTAL CONDITIONS:
     AMBIENT ROOM TEMPERATURE= 22 C
     AMBIENT ATMOSPHERIC PRESSURE= 1.005 Atm
     MEAN REACTOR TEMPERATURE= 850 C
     MEAN REACTOR PRESSURE= 1.128 Atm
     NUMBER OF REACTOR INSERTS= 12
     NITROGEN TRANSPORT GAS TEMPERATURE= 21.5 C
     BIOMASS FLOWRATE= 4.05000001E-05 kg/s (2.43 g/min)
     THERMOFOR (solids) FLOWRATE= 0 kg/s (0 g/min)

SOLIDS LOADING:
     BIOMASS LOADING (solids/gas) = .357
     THERMOFOR LOADING (solids/gas)= 0

MASS FLOWRATES OF NITROGEN TRANSPORT GAS:
     BIOMASS N2 TRANSPORT GAS= 1.1342181E-04 kg/s (6.805 g/min)
     THERMOFOR N2 TRANSPORT GAS= 0 kg/s (0 g/min)
     BIOMASS/THERMOFOR EXTRA N2= 8.01554905E-04 kg/s (48.093 g/min)
     CRYOFOR EXTRA N2= 3.79579221E-04 kg/s (22.775 g/min)
     TOTAL N2 FLOW TO RECOVERY TRAIN= 1.29455594E-03 kg/s (77.673 g/min)
     TOTAL N2 FLOW THROUGH REACTOR= 9.14976715E-04 kg/s (54.899 g/min)

RESIDENCE TIME:
     REACTOR RESIDENCE TIME (incl. thermovort.)= 64.902 ms
     PORTION OF RESIDENCE TIME DUE TO BIOMASS N2= 12.15 %
     PORTION OF RESIDENCE TIME DUE TO THERMOFOR N2= 0 %
     PORTION OF RESIDENCE TIME DUE TO BIOMASS/THERMOFOR EXTRA N2= 85.865 %
     PORTION OF RESIDENCE TIME DUE TO PRODUCT GAS= 1.985 %

REYNOLDS NUMBERS:
     REACTOR REYNOLDS NUMBER= 1278.1    VELOCITY= 7.9 m/s
     REACTOR INSERT/TV EXIT REYNOLDS NUMBER= 2605.7   VELOCITY= 32.7 m/s
     BIOMASS INLET = 1137.3  VELOCITY= 4.2 m/s
     THERMOFOR INLET = 4941.8  VELOCITY= 110.9 m/s

COMMENTS:
     NO THERMOFOR SOLIDS WERE INJECTED.
     REACTOR VOLUME = f (TEMP.)
```

RUN CK-214: GAS PRODUCT SUMMARY

REACTOR TEMP. = 950 C
RESIDENCE TIME =65 ms

TABLE 1. G.C. CALIBRATION SUMMARY

GAS COMPONENT	AVG CAL. AREA	AVG RF	AVG PEAK AREAS FOR ULTRAPYROLYSIS GAS SAMPLES				
			DYNAMIC	BAG 1	BAG 2	BAG 3	BAG 4
HYDROGEN	79813	10195.9	0	5403	5346	6201	0
CARB DIOX	116531	51335.2	0	4927.5	5311.5	5237	0
ETHYLENE	62095	54469.3	0	9260.5	10147	9894	0
ETHANE	31323	58005.6	0	1528	1264.5	1453	0
ACETYLENE	23635	46343.6	0	2415	2679	2583	0
OXYGEN	16612	31964.6	0	9127	7850.5	12132	0
NITROGEN	3165470	42060.7	0	3998079	3985712	3973879	0
METHANE	74823	34964.1	0	5810.5	6209	5961	0
CARB MONOX	362092	43625.5	0	65907	72057.5	69104	0
BENZ/TOL	3905	98786.8	0	1123	1320	1126	0
PROPANE	40757	78376.1	0	0	0	0	0
PROPYLENE	38953	74510.3	0	1627	1828	1857	0
BUTENE-1	49158	38741.2	0	0	0	0	0

TABLE 2. G.C. COMPOSITION SUMMARY (Molar %)

GAS COMPONENT	ACTUAL G.C. MOLAR COMPOSITION					AIR FREE MOLAR COMPOSITION				
	DYNAMIC	BAG 1	BAG 2	BAG 3	BAG 4	DYNAMIC	BAG 1	BAG 2	BAG 3	BAG 4
HYDROGEN	0	.53	.524	.59	0	0	.549	.547	[illegible]	0
CARB DIOX	0	.095	.103	.102	0	0	.099	.107	.106	0
ETHYLENE	0	.17	.186	.182	0	0	.176	.193	.19	0
ETHANE	0	.026	.022	.025	0	0	.027	.023	.026	0
ACETYLENE	0	.052	.058	.056	0	0	.054	.06	.058	0
OXYGEN	0	.286	.246	.39	0	0	0	0	0	0
NITROGEN	0	95.06	94.761	94.479	0	0	97.324	97.142	[illegible]	0
METHANE	0	.166	.175	.17	0	0	.172	.184	.178	0
CARB MONOX	0	1.511	1.652	1.594	0	0	1.564	1.71	1.653	0
BENZ/TOL	0	.011	.013	.011	0	0	.012	.014	.012	0
PROPANE	0	0	0	0	0	0	0	0	0	0
PROPYLENE	0	.022	.024	.025	0	0	.022	.025	.026	0
BUTENE-1	0	0	0	0	0	0	0	0	0	0
TOTAL	0	97.93	97.767	97.621	0	0	100	100	100	0
MOL. WT	0	27.32	27.27	27.22	0	0	27.39	[illegible]	27.34	0

RUN CK-314 (cont'd)

TABLE 3. SUMMARY OF PRODUCT GAS COMPOSITION

GAS COMPONENT	MOL. WT.	NITROGEN/OXYGEN FREE MOLAR COMPOSITION					PRODUCT GAS AVG (3 BAGS)			SPECIFIC GAS YIELD *
							MOLAR %		MASS	
		DYNAMIC	BAG 1	BAG 2	BAG 3	BAG 4	AIR-FREE	N/O FREE	FRACTION	
HYDROGEN	2.02	0	20.504	18.992	22.01	0	.576	20.523	.013	.011
CARB DIOX	44.01	0	3.714	3.748	3.692	0	.104	3.718	.072	.045
ETHYLENE	28.05	0	6.578	6.748	6.573	0	.186	6.633	.091	.051
ETHANE	30.07	0	1.019	.79	.906	0	.025	.903	.012	7E-03
ACETYLENE	26.04	0	2.016	2.094	2.017	0	.057	2.042	.023	.014
OXYGEN	32	0	0	0	0	0	0	0	0	0
NITROGEN	28.02	0	0	0	0	0	97.194	0	0	0
METHANE	16.04	0	6.43	6.432	6.17	0	.178	6.34	.044	.028
CARB MONOX	28.01	0	58.455	59.827	57.323	0	1.642	58.52	.717	.447
BENZ/TOL	85.13	0	.442	.486	.414	0	.013	.447	.017	.01
PROPANE	44.09	0	0	0	0	0	0	0	0	0
PROPYLENE	42.08	0	.84	.884	.895	0	.025	.874	.016	.01
BUTENE-1	56.1	0	0	0	0	0	0	0	0	0
TOTAL		0	100	100	100	0	100	100	1	.623
MOL WT.		0	22.86	23.28	22.49	0	27.88	22.87		

* mass yield of the gaseous component per unit mass of dry biomass

TABLE 4. YIELD OF GAS IN EACH SAMPLE BAG

	BAG 1	BAG 2	BAG 3	BAG 4	TOTAL
TANK DP (Atm)	.418	.414	.43	0	1.262
NO. MOLES (AF)	7.459	7.364	7.605	0	22.428
MASS (gm AF)	208	205.3	211.9	0	625.2
NO. MOLES (N/O FREE)	.2	.21	.219	0	.629
PRODUCT GAS (gm)	4.56	4.9	4.93	0	14.4

RUN CK-314 (cont'd)

TABLE 5. MASS BALANCE (NO SOLVENT/WATER SOLVENTS)

COMPONENT	MASS (gm)
BIOMASS (as is)	23.3
DRY BIOMASS	23.09
GAS	14.4
WATER (by K-F) *	N/A
VOLATILES	0
TAR	0
CHAR	0
TOTAL INPUT	23.3
TOTAL OUTPUT	14.4

MASS BALANCE (products/biomass) = 61.8 %
FRACTIONAL CONVERSION ('as is' biomass to gas) = .618
FRACTIONAL CONVERSION (dry biomass to gas) = .623

* Water Predicted By Shift Equilibrium (gm) = 3E-03

TABLE 6. ELEMENTAL BALANCE

ELEMENT	DRY BIOMASS INPUT	DRY GAS OUTPUT
CARBON	10.26	7.05
HYDROGEN	1.44	.7
OXYGEN	11.39	6.64

CARBON BALANCE (carbon in gas/feedstock carbon) = 68.7 %

Mass Balance Summary Sheet
****

Run: CK-314 Temperature: 850 C Residence Time: 50 ms

1. Pure Liquid Sample:

	Mass before (g)	Mass after (g)	Difference (g)
Condenser	3742.5	3741.4	1.1

Weight of pure condenser sample (if any) for analysis = NONE g

2. Solid Residue:

	Mass before (g)	Mass after (g)	Difference (g)
Filter Paper	1.25	1.59	0.34

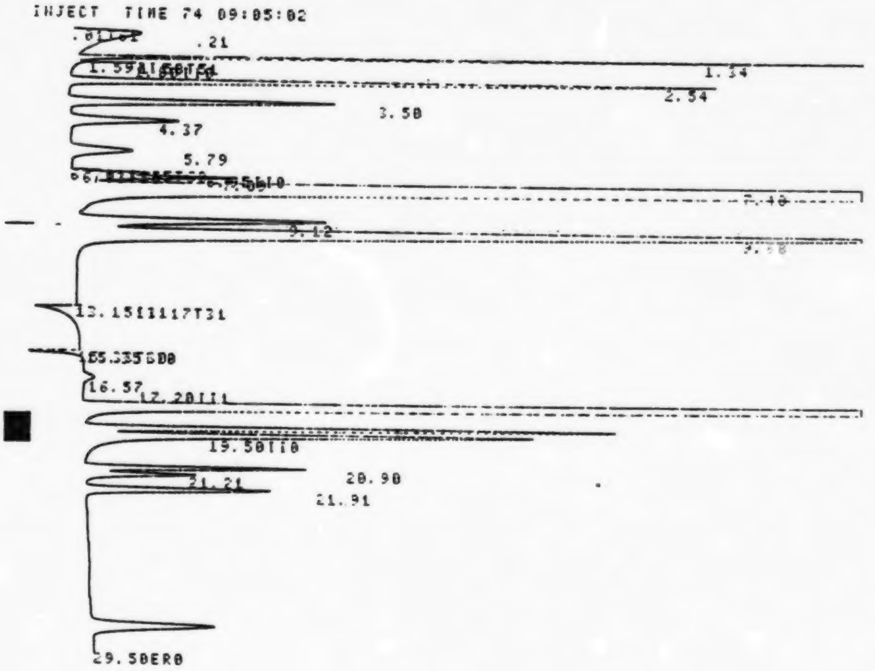
3. Roto-vaporation:

	Mass of Flask (g)	Flask + Organics (g)	Difference (g)
All system (MeOH)	357.1	364.8	7.7
		TOTAL	

4. Summary:

G.C. VOLATILES ("liquids")	0,28			
Total Solids Collected --->	0.34	g	1.46	%
Total Organic Liquids ---->	7.7	g	33.05	%
Total Collected ---------->	8.32	g		
Gas Produced ------------->	14.4	g	61.80	%
Total Products ----------->	22.72	g		
Mass of Biomass Fed ------>	23.3	g		
Mass Percentage Recovered	97.4	%		

Date: ________



```
DUAL
FILE 2      METHOD  5.      RUN ***      INDEX 749

ANALYST: 7

NAME                CONC        RT       AREA BC       RF

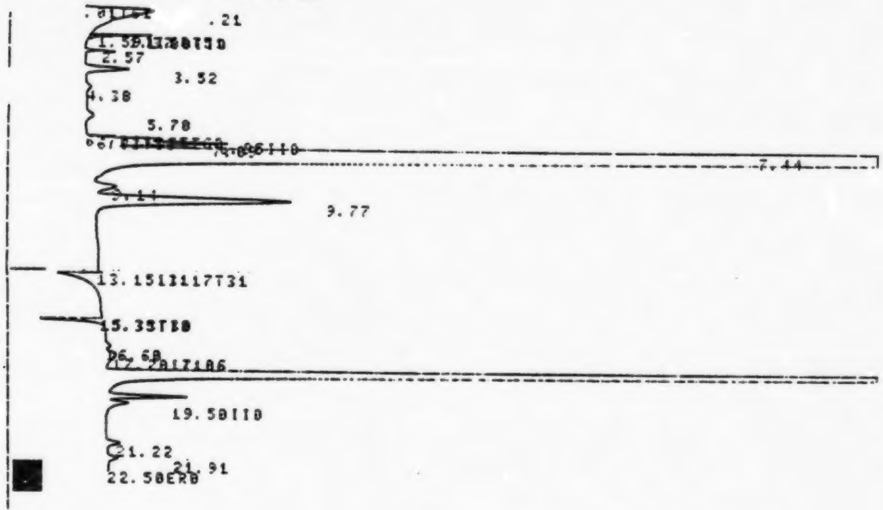
HYDROGEN             0.        1.34     79916 23
CARB DIOX            0.        2.54    116659 01
ETHYLENE             0.        3.5      61914 01
ETHANE               0.        4.37     31654 01
ACETYLENE            0.        5.79     22747 01
OXYGEN               0.        7.09     16580 01
NITROGEN             0.        7.40   3173239 01
METHANE              0.        9.12     74940 02
CARB MONOX           0.        9.68    363490 03
BENZ/TOL             0.       16.57      3950 01
PROPANE              0.       20.9      40707 02
ACETYLENE            0.       21.21     23801 03
PROPYLENE            0.       21.91     38829 01

TOTALS               0.               4048426
```

Sample Chromatogram: CK-314 Calibration Gas.

```
FI=2

INJECT  TIME 74 11:48:23
```



```
DUAL
FILE 2      METHOD  5.      RUN ***     INDEX 752

ANALYST: 7

NAME                 CONC         RT       AREA BC       RF

HYDROGEN              0.         1.37      6201 23
CARB DIOX             0.         2.57      5273 01
ETHYLENE              0.         3.52      9976 01
ETHANE                0.         4.38      1305 01
ACETYLENE             0.         5.78      2505 01
OXYGEN                0.         7.09     12171 01
NITROGEN              0.         7.44   3977841 01
METHANE               0.         9.14      5794 02
CARB MONOX            0.         9.77     69140 03
BENZ/TOL              0.        16.6       1126 02
 12                   0.        17.86      2326 23
ACETYLENE             0.        21.22      2583 01
PROPYLENE             0.        21.91      1852 01

TOTALS                0.                4098093
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Sample Chromatogram: CK-314 Product Gas Sample.

14.4 Cellulose Pyrolysis: Gas Yield Curves

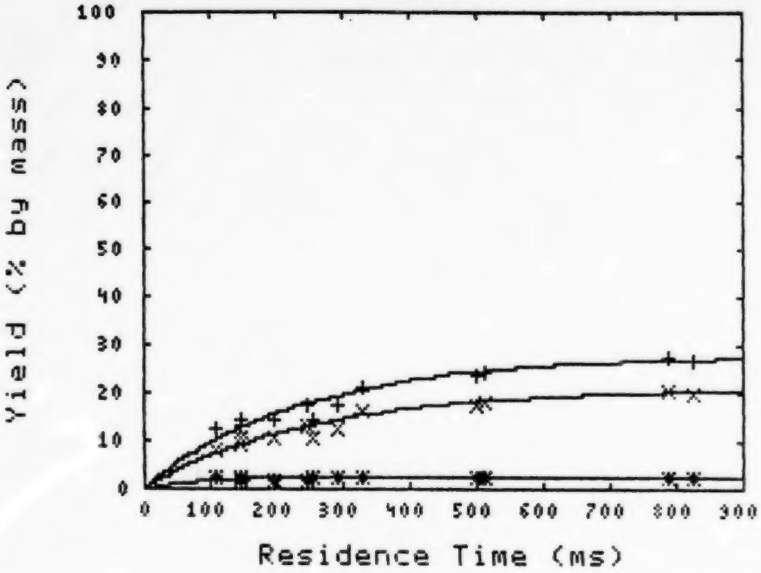

Figure 14.4.1 Fast Pyrolysis of Cellulose (650 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

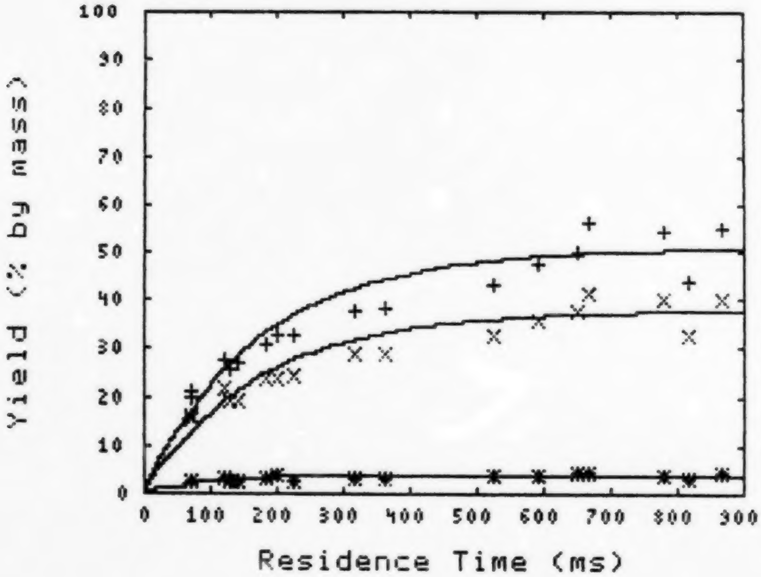

Figure 14.4.2 Fast Pyrolysis of Cellulose (700 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

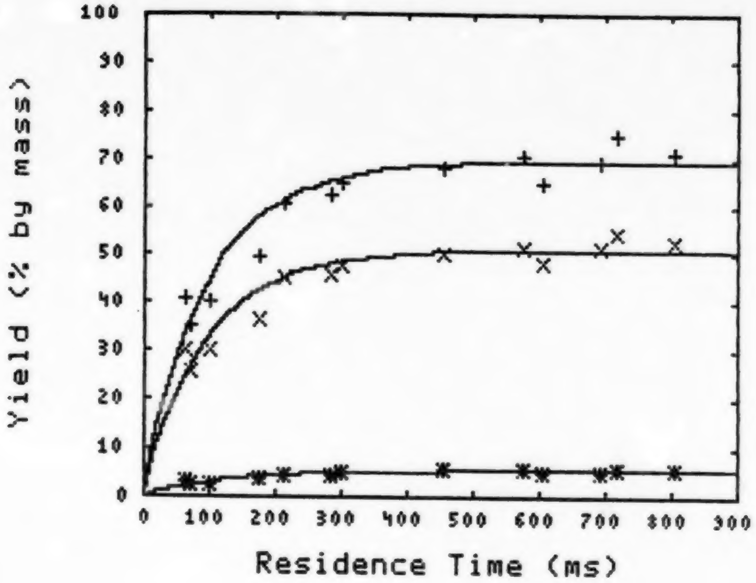

Figure 14.4.3 Fast Pyrolysis of Cellulose (750 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

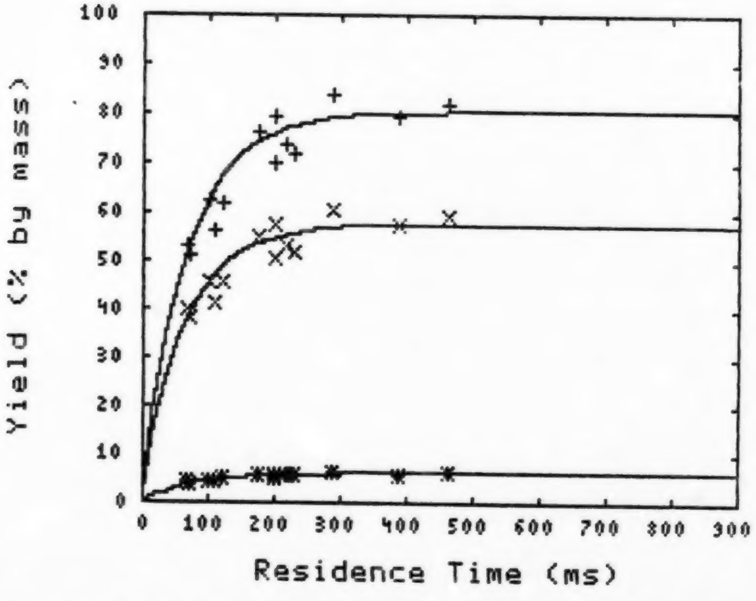

Figure 14.4.4 Fast Pyrolysis of Cellulose (800 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

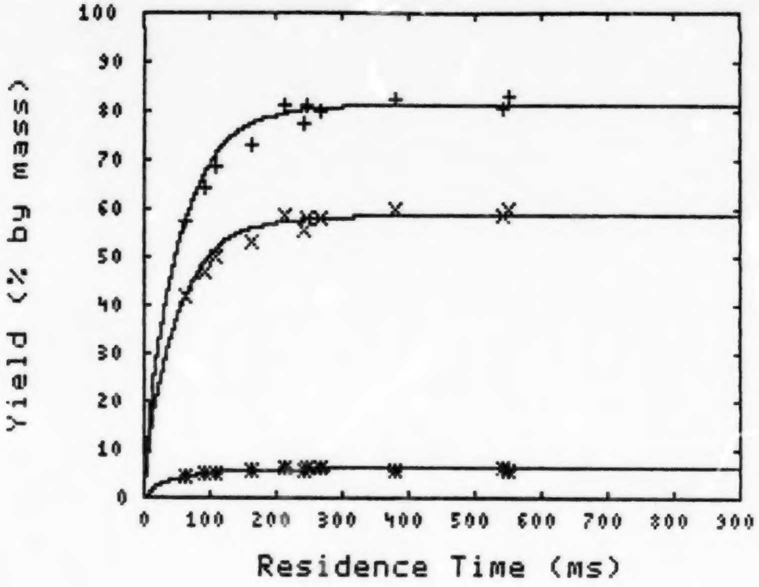

Figure 14.4.5 Fast Pyrolysis of Cellulose (825 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

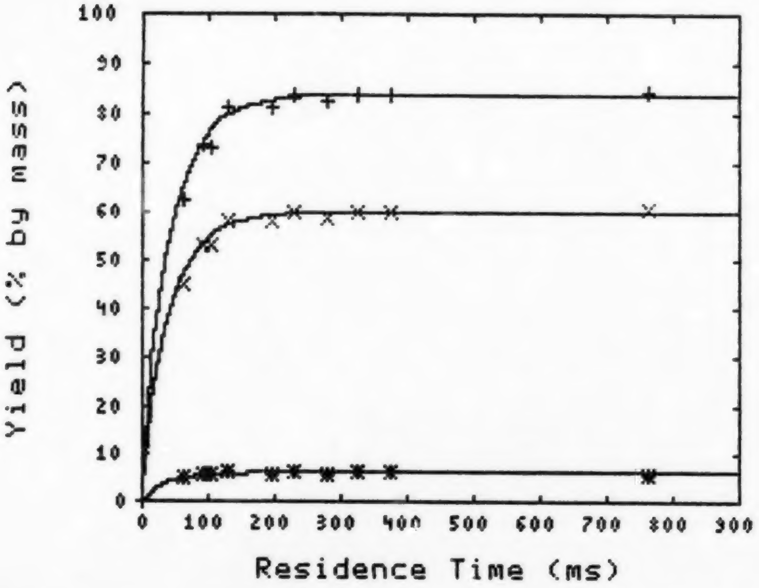

Figure 14.4.6 Fast Pyrolysis of Cellulose (850 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

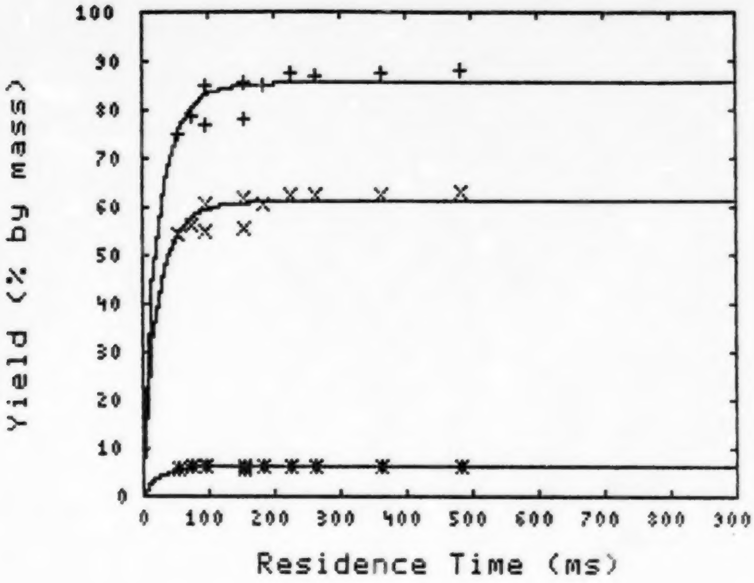

Figure 14.4.7 Fast Pyrolysis of Cellulose (875 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

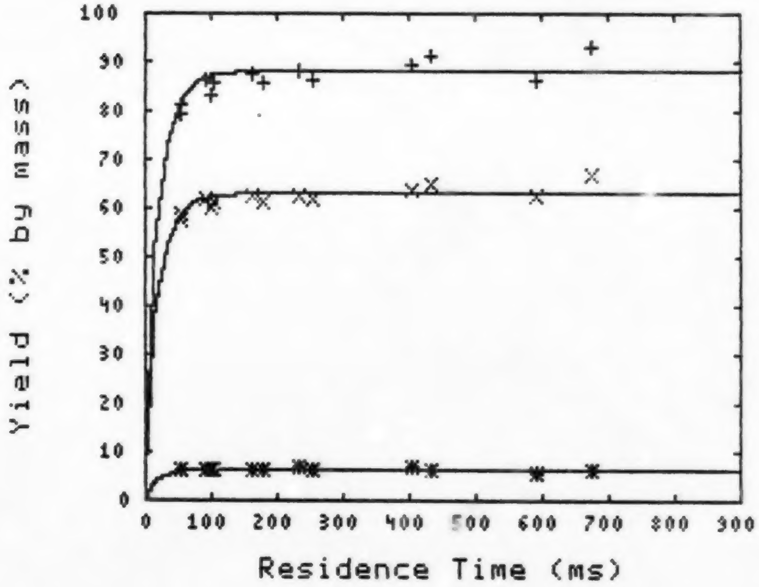

Figure 14.4.8 Fast Pyrolysis of Cellulose (900 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

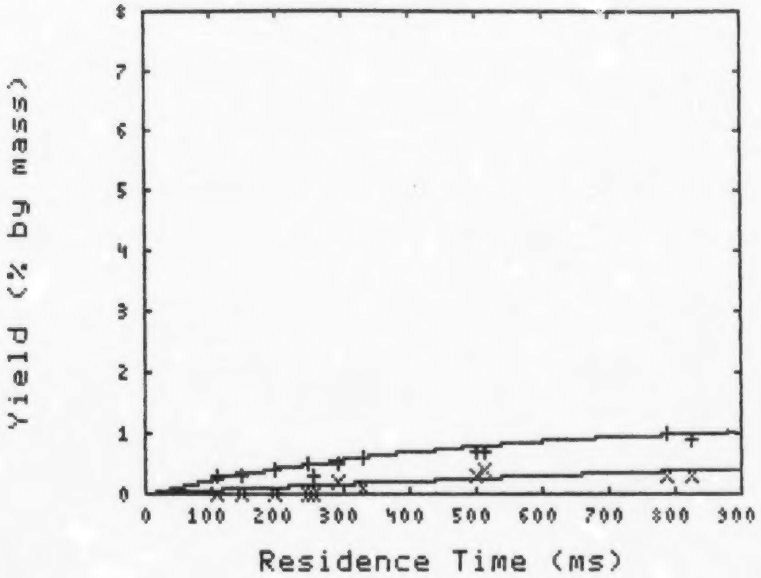

Figure 14.4.9 Fast Pyrolysis of Cellulose (650 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

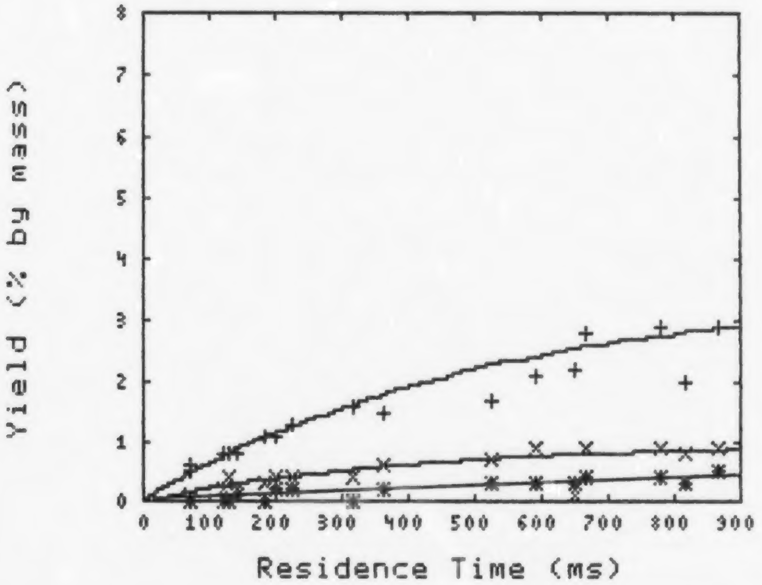

Figure 14.4.10 Fast Pyrolysis of Cellulose (700 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

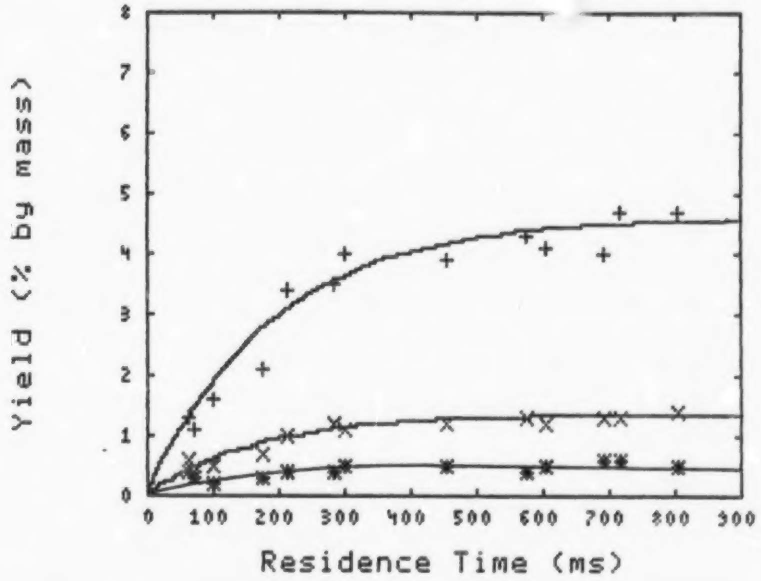

Figure 14.4.11 Fast Pyrolysis of Cellulose (750 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

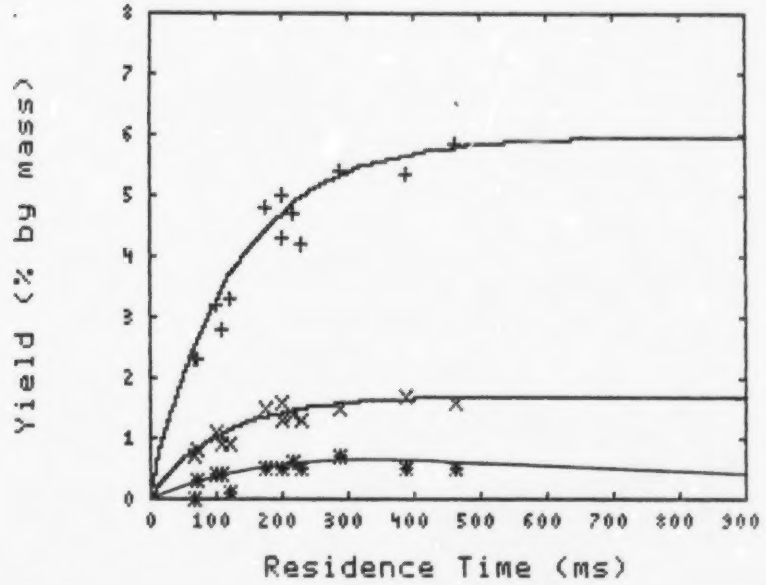

Figure 14.4.12 Fast Pyrolysis of Cellulose (800 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

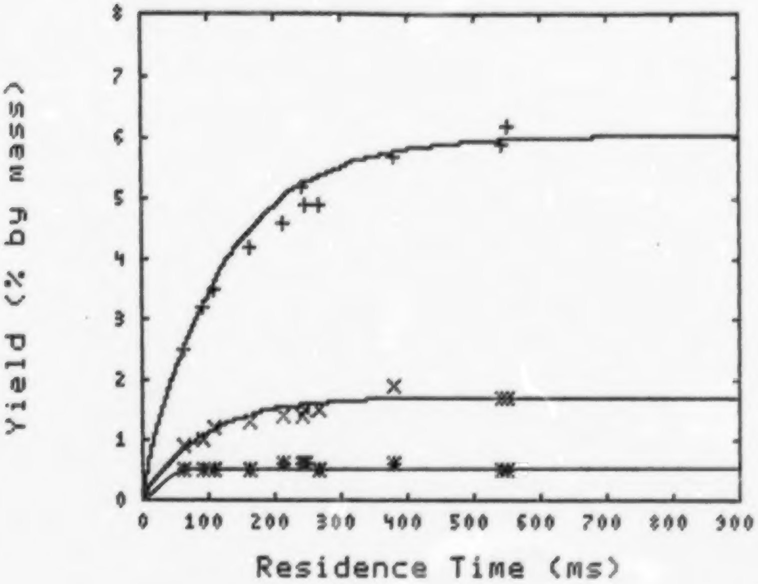

Figure 14.4.13 Fast Pyrolysis of Cellulose (825 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

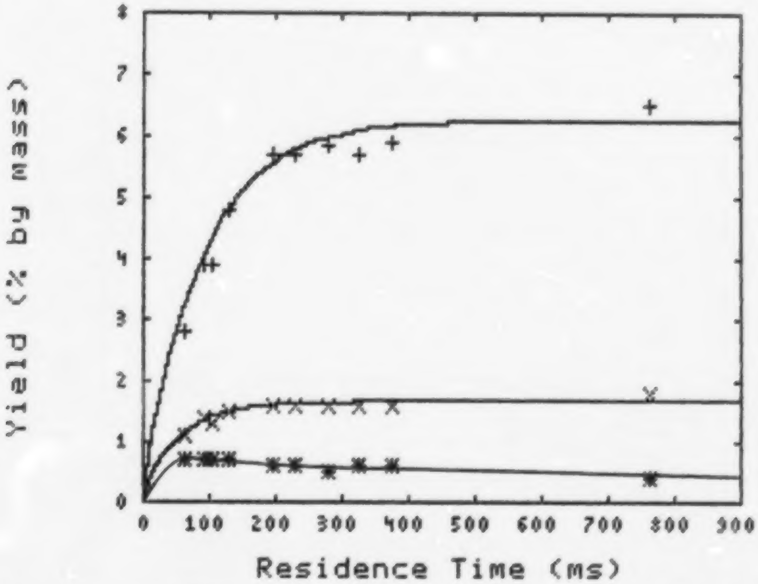

Figure 14.4.14 Fast Pyrolysis of Cellulose (850 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

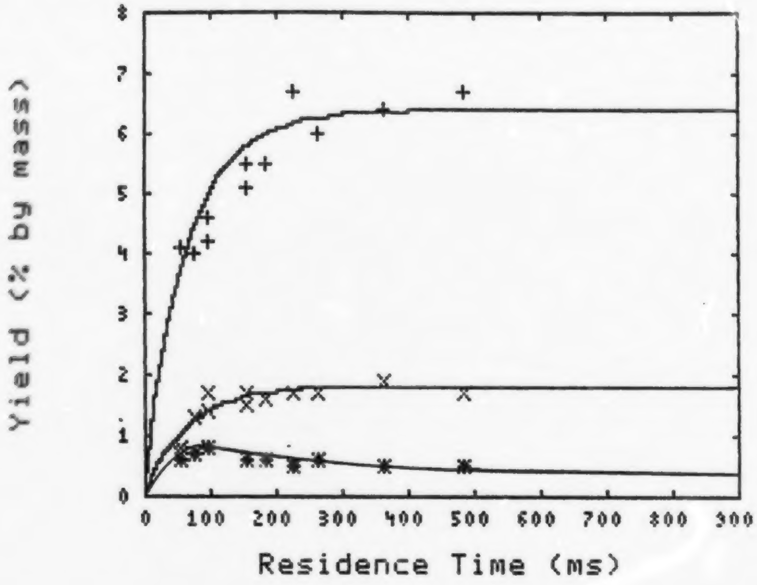

Figure 14.4.15 Fast Pyrolysis of Cellulose (875 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

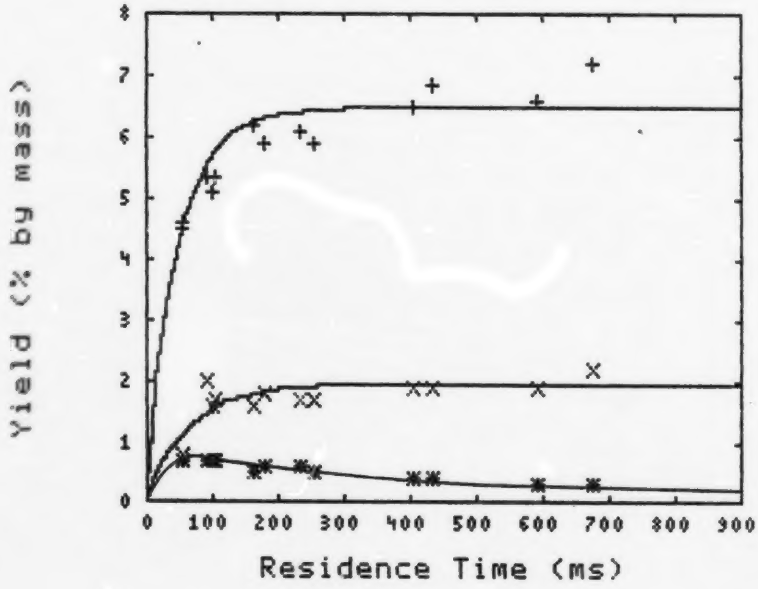

Figure 14.4.16 Fast Pyrolysis of Cellulose (900 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

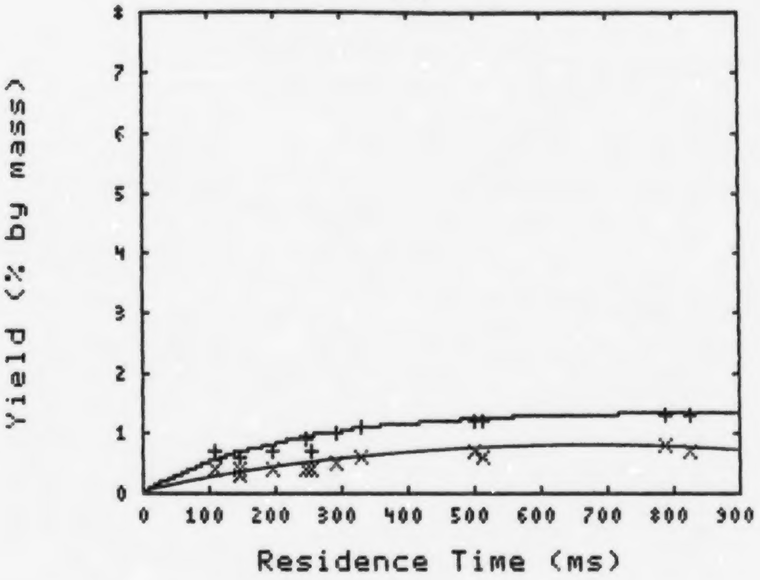

Figure 14.4.17 Fast Pyrolysis of Cellulose (650 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

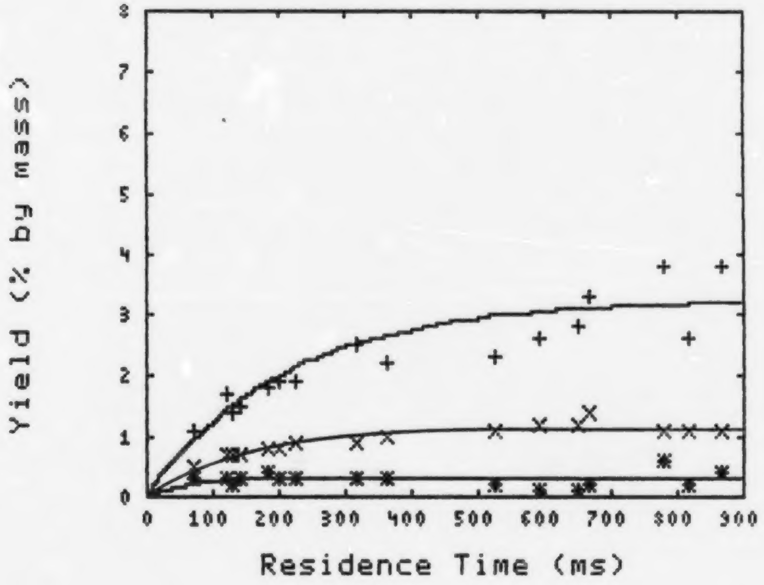

Figure 14.4.18 Fast Pyrolysis of Cellulose (700 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

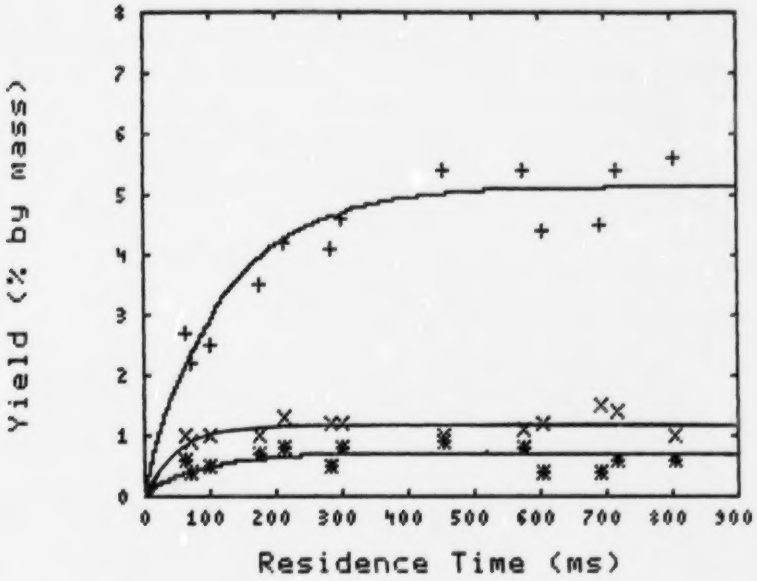

Figure 14.4.19 Fast Pyrolysis of Cellulose (750 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

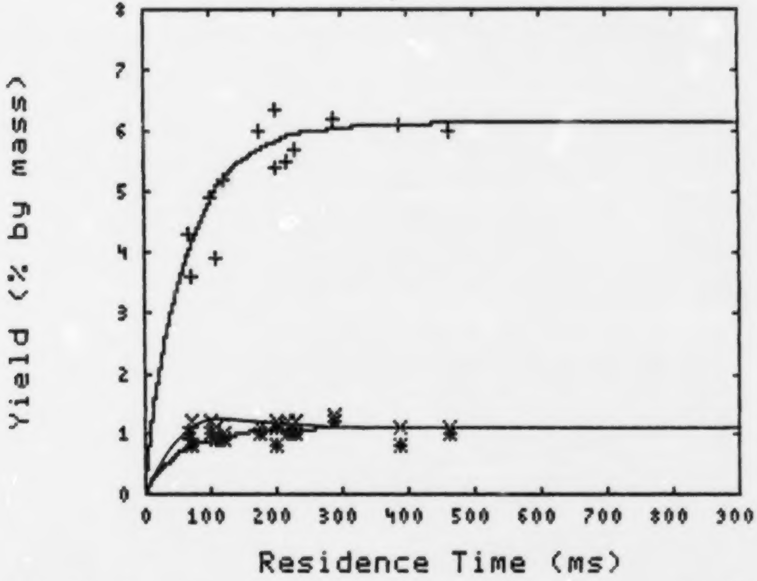

Figure 14.4.20 Fast Pyrolysis of Cellulose (800 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

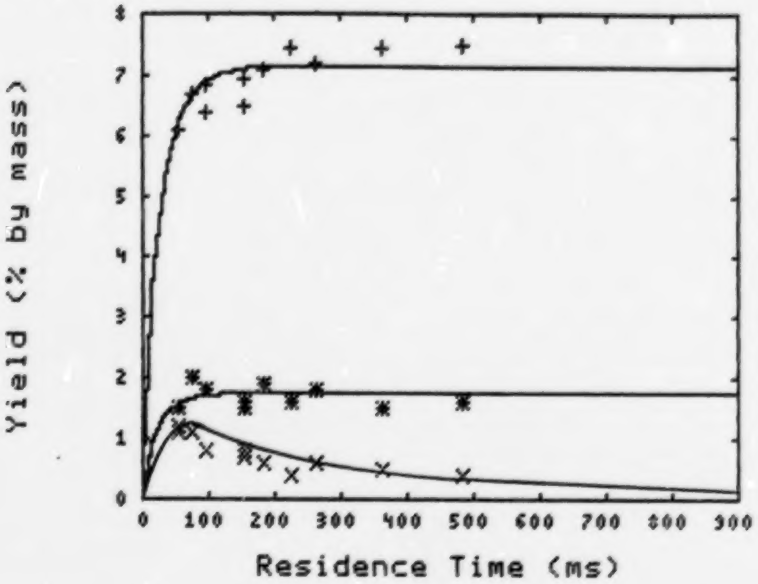

Figure 14.4.21 Fast Pyrolysis of Cellulose (825 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

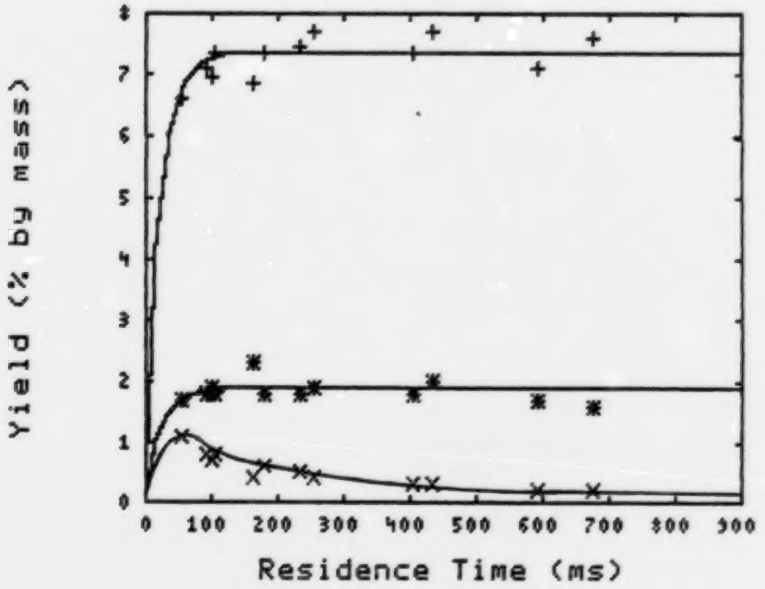

Figure 14.4.22 Fast Pyrolysis of Cellulose (850 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

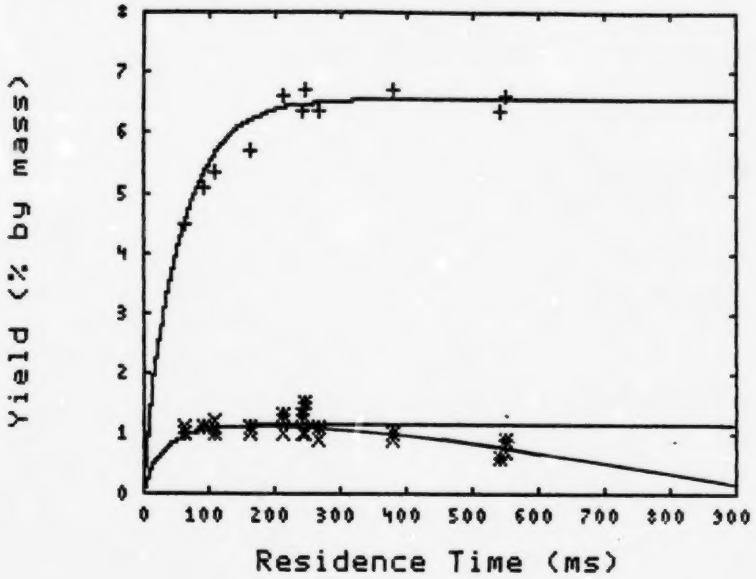

Figure 14.4.23 Fast Pyrolysis of Cellulose (875 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

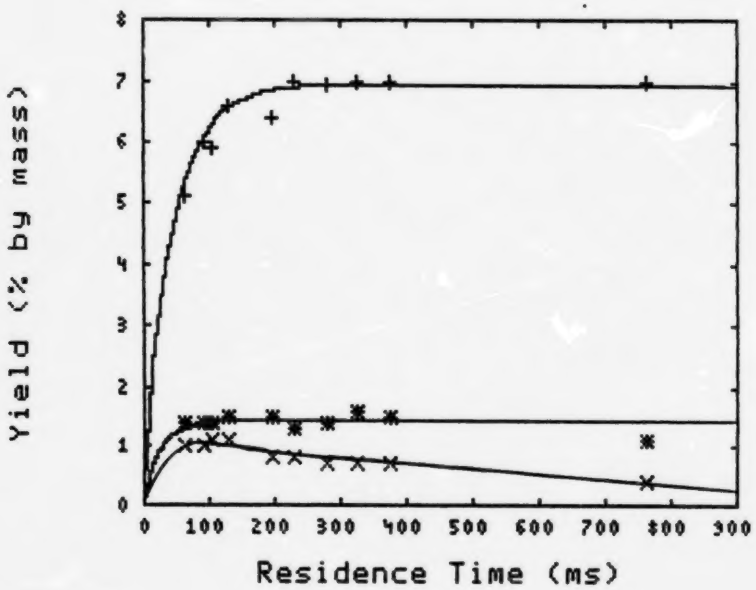

Figure 14.4.24 Fast Pyrolysis of Cellulose (900 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

14.5 IEA Poplar Pyrolysis: Gas Yield Curves

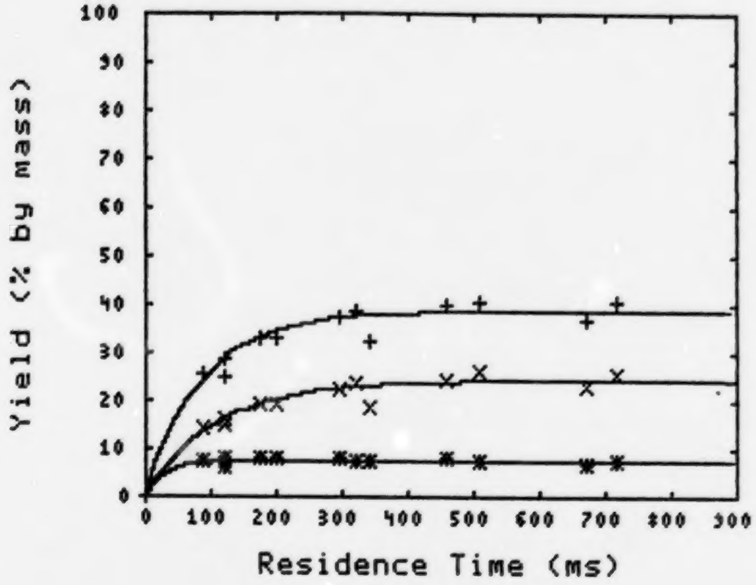

Figure 14.5.1 Fast Pyrolysis of IEA Poplar (700 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

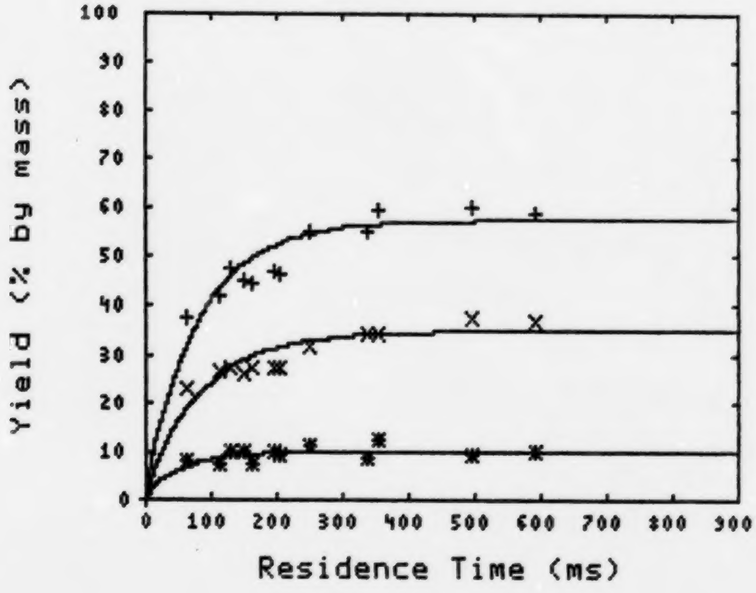

Figure 14.5.2 Fast Pyrolysis of IEA Poplar (750 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

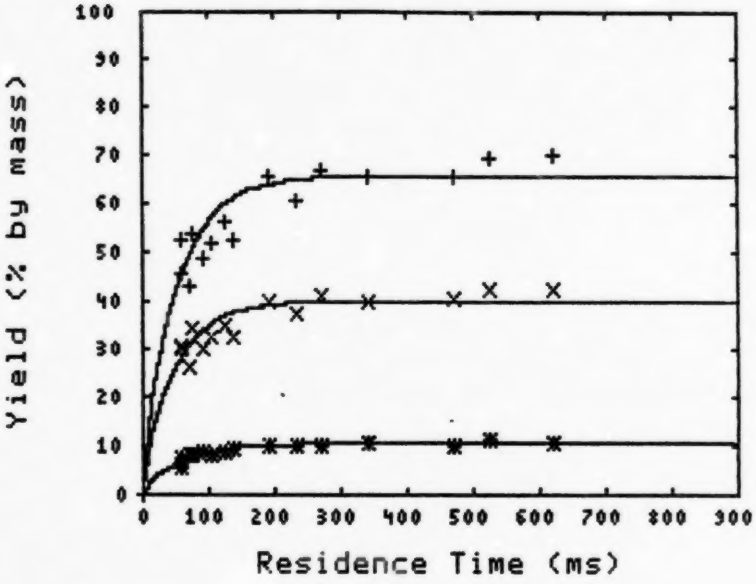

Figure 14.5.3 Fast Pyrolysis of IEA Poplar (800 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

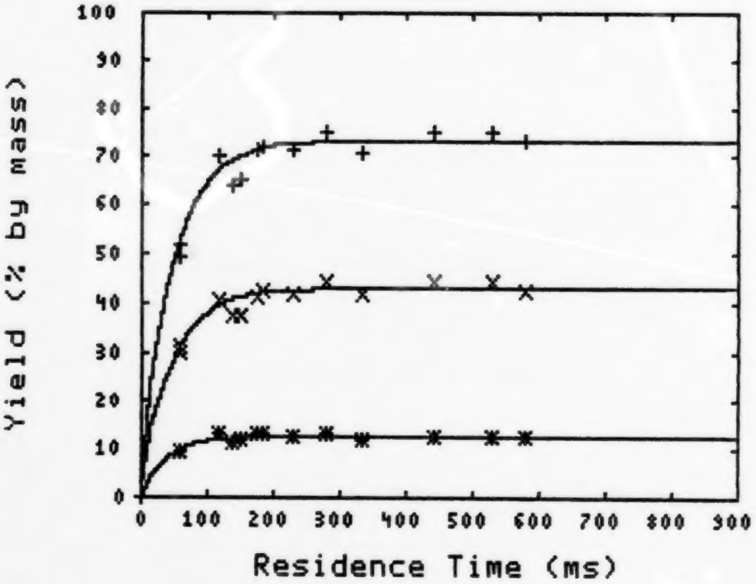

Figure 14.5.4 Fast Pyrolysis of IEA Poplar (825 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

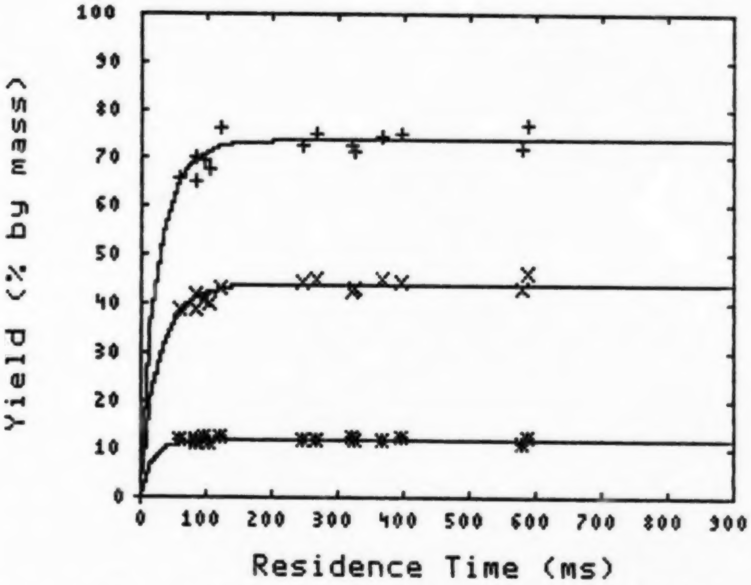

Figure 14.5.5 Fast Pyrolysis of IEA Poplar (850 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

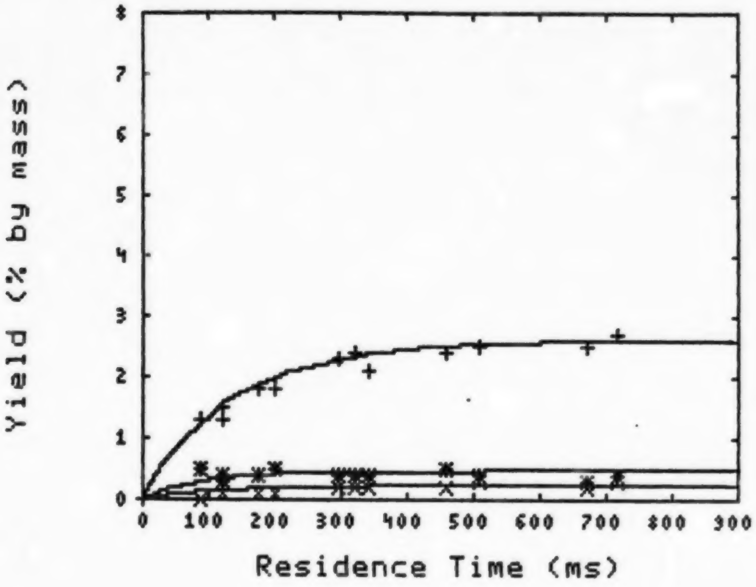

Figure 14.5.6 Fast Pyrolysis of IEA Poplar (700 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

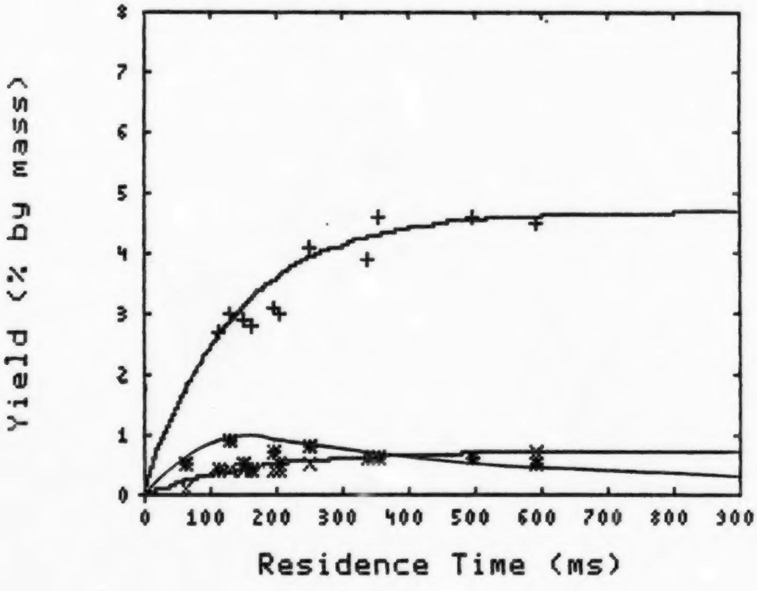

Figure 14.5.7 Fast Pyrolysis of IEA Poplar (750 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

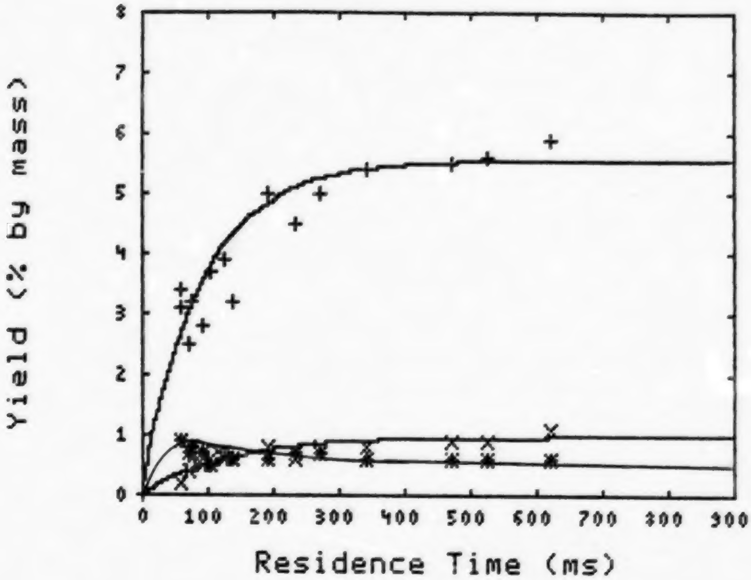

Figure 14.5.8 Fast Pyrolysis of IEA Poplar (800 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

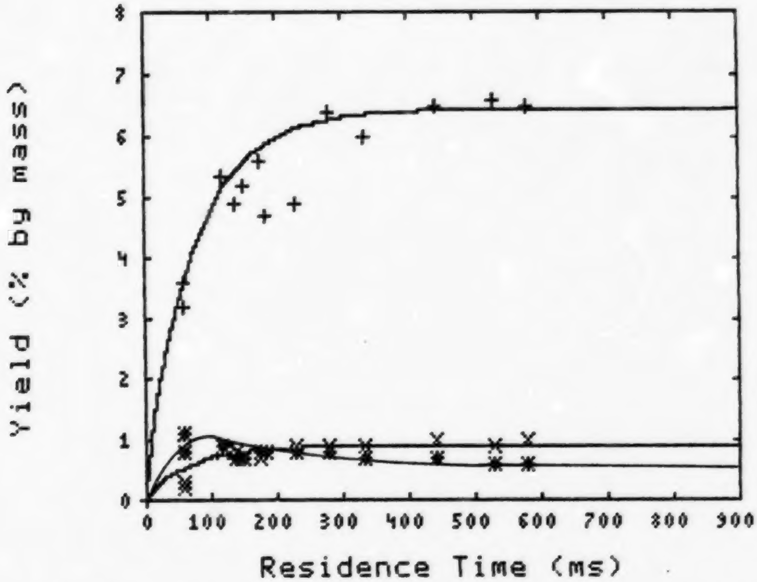

Figure 14.5.9 Fast Pyrolysis of IEA Poplar (825 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

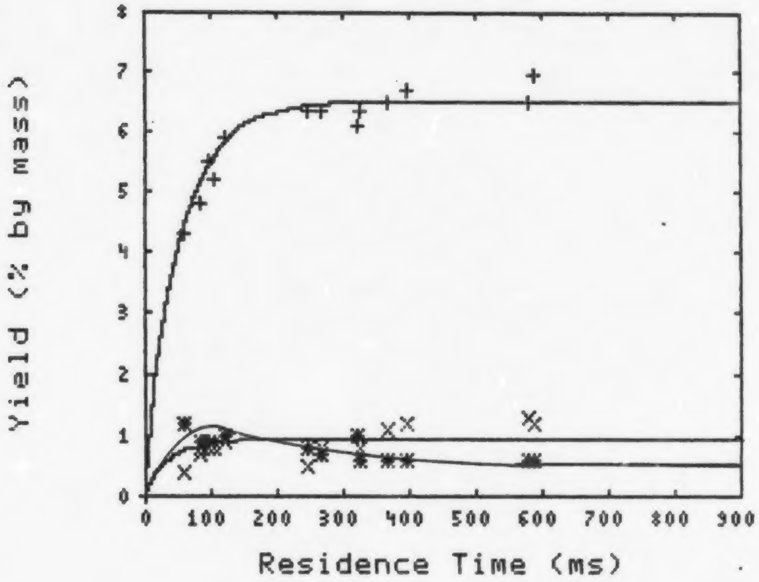

Figure 14.5.10 Fast Pyrolysis of IEA Poplar (850 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

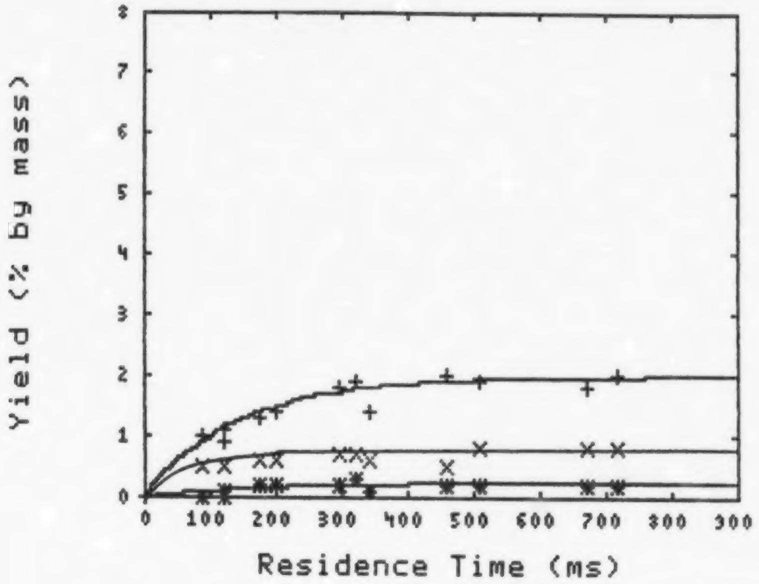

Figure 14.5.11 Fast Pyrolysis of IEA Poplar (700 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

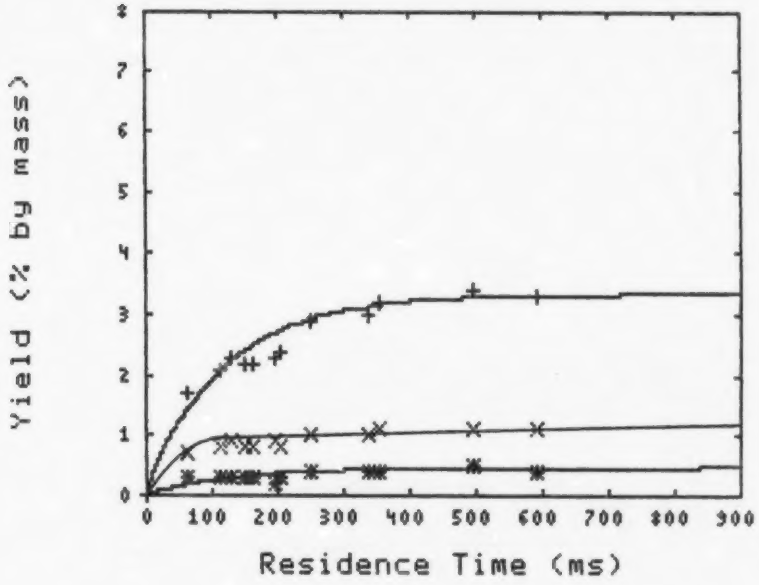

Figure 14.5.12 Fast Pyrolysis of IEA Poplar (750 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

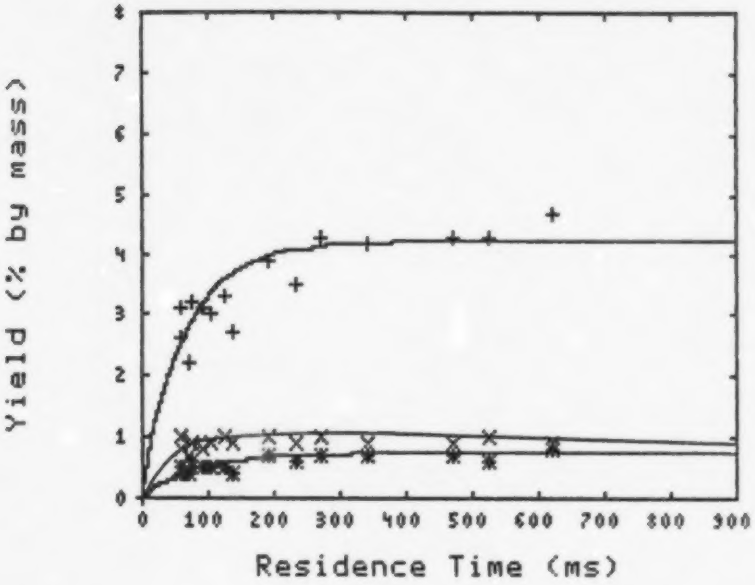

Figure 14.5.13 Fast Pyrolysis of IEA Poplar (800 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

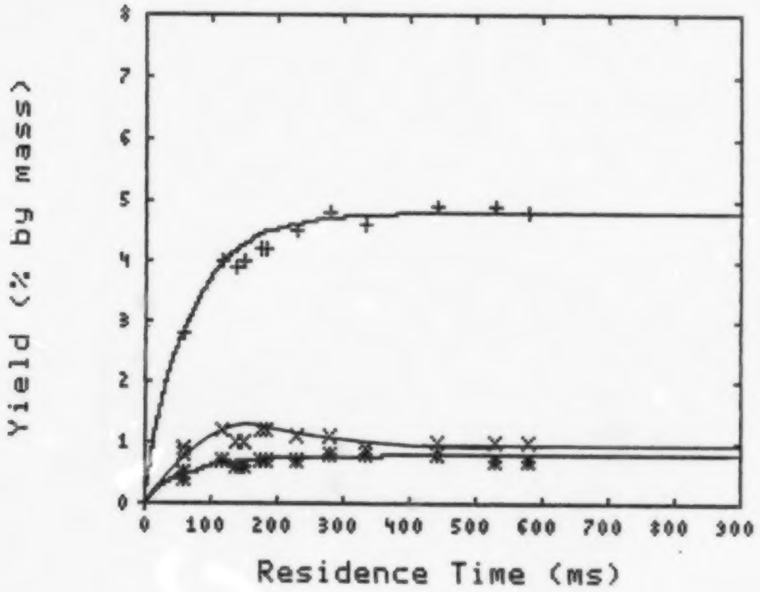

Figure 14.5.14 Fast Pyrolysis of IEA Poplar (825 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

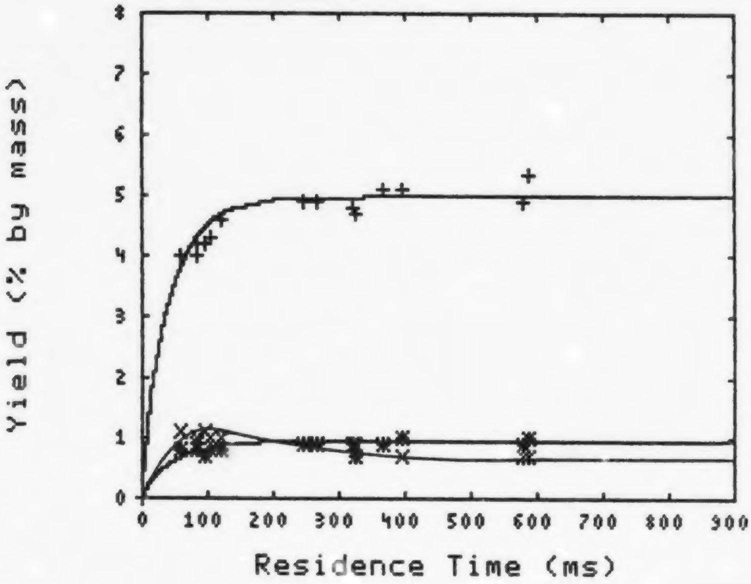

Figure 14.5.15 Fast Pyrolysis of IEA Poplar (850 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

14.6 Red Maple Pyrolysis: Gas Yield Curves

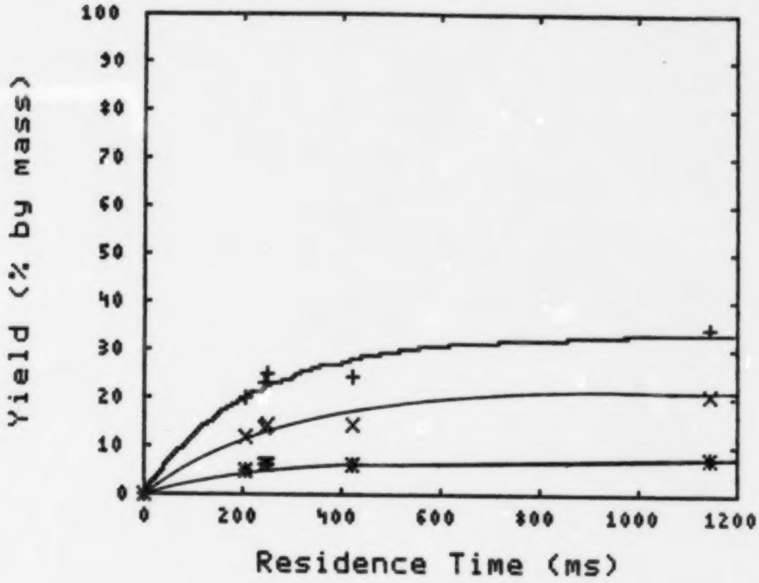

Figure 14.6.1 Fast Pyrolysis of Red Maple (650 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

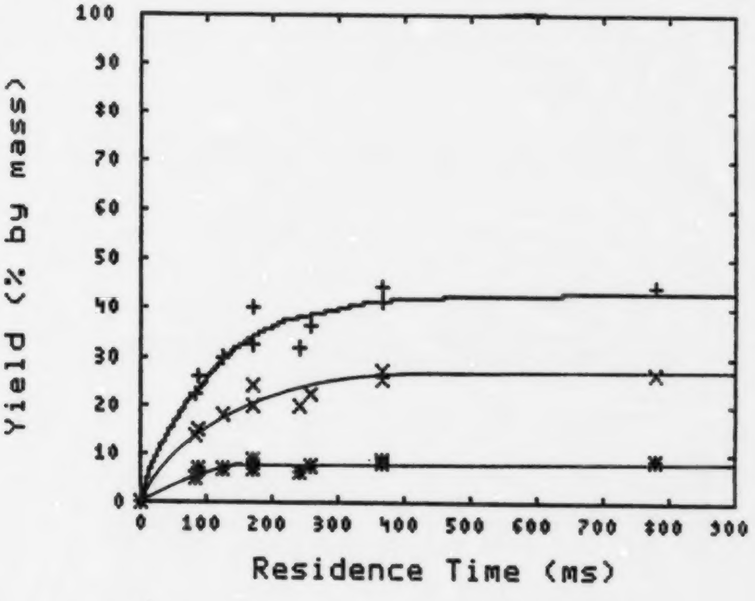

Figure 14.6.2 Fast Pyrolysis of Red Maple (700 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

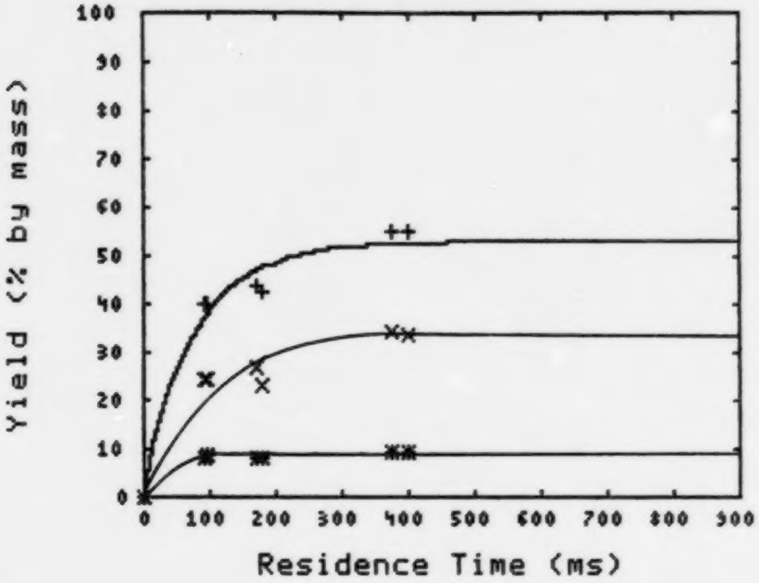

Figure 14.6.3 Fast Pyrolysis of Red Maple (750 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

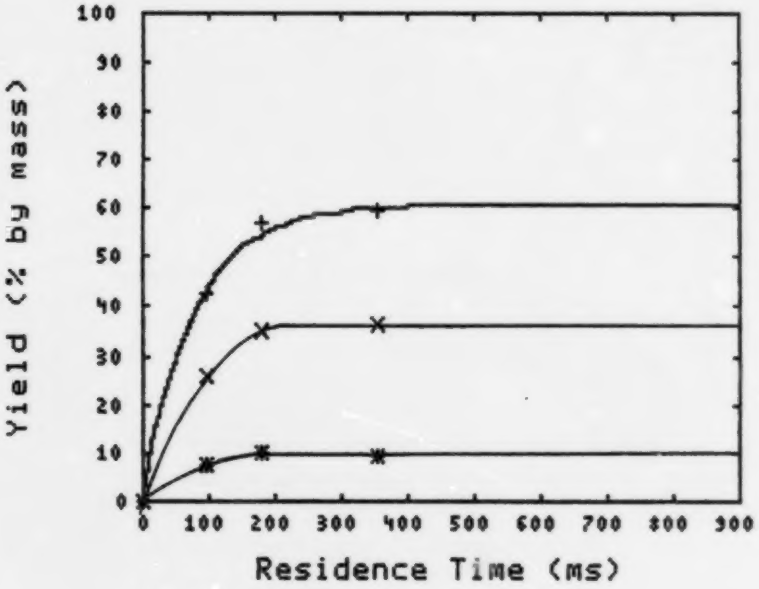

Figure 14.6.4 Fast Pyrolysis of Red Maple (800 C): Total Gas (+), Carbon Monoxide (X) and Carbon Dioxide (*) Yields vs Residence Time.

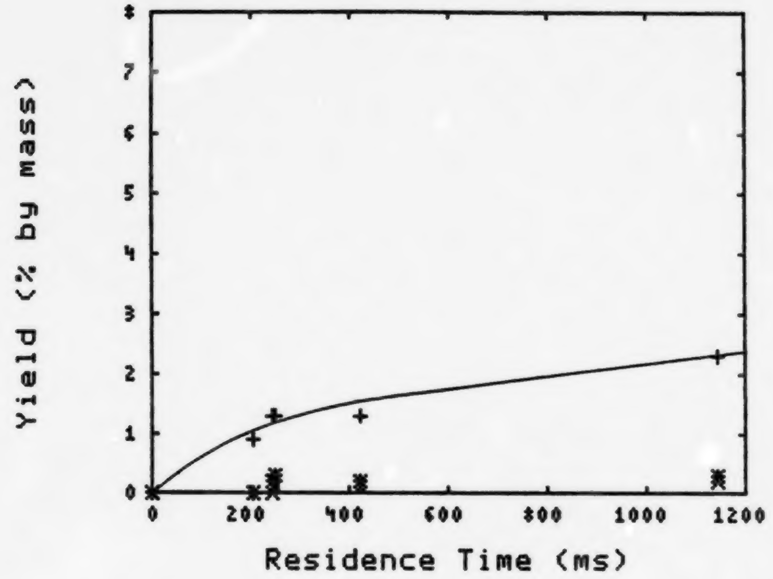

Figure 14.6.5 Fast Pyrolysis of Red Maple (650 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

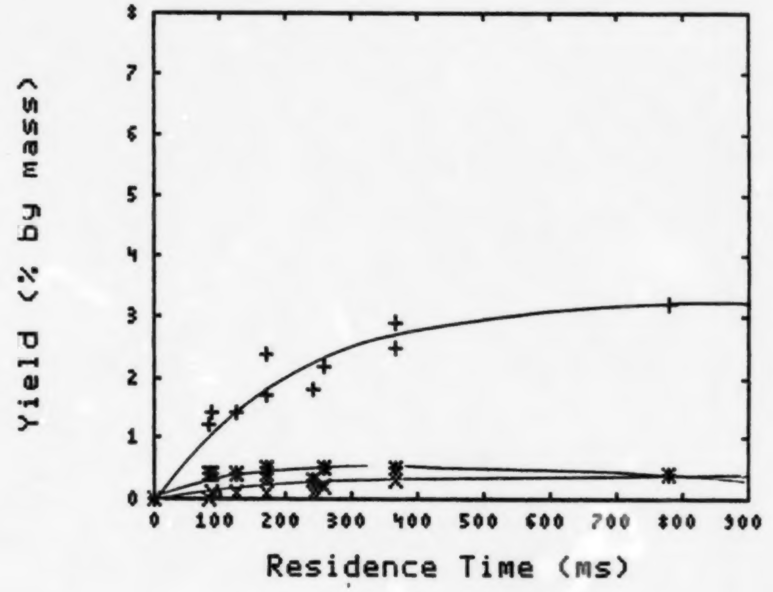

Figure 14.6.6 Fast Pyrolysis of Red Maple (700 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

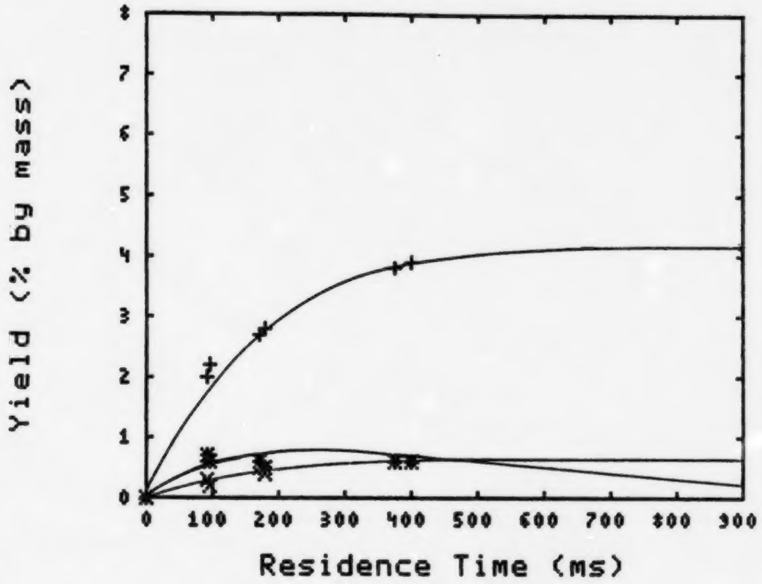

Figure 14.6.7 Fast Pyrolysis of Red Maple (750 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

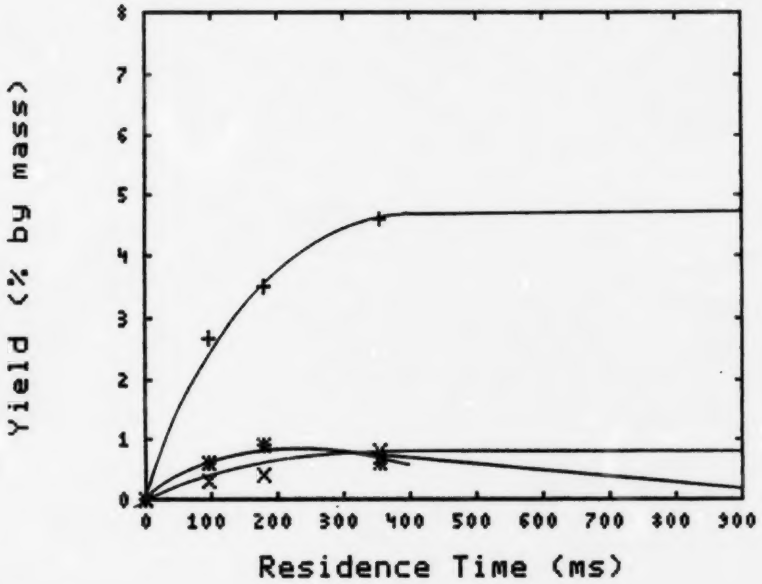

Figure 14.6.8 Fast Pyrolysis of Red Maple (800 C): Methane (+), Hydrogen (X) and Ethane (*) Yields vs Residence Time.

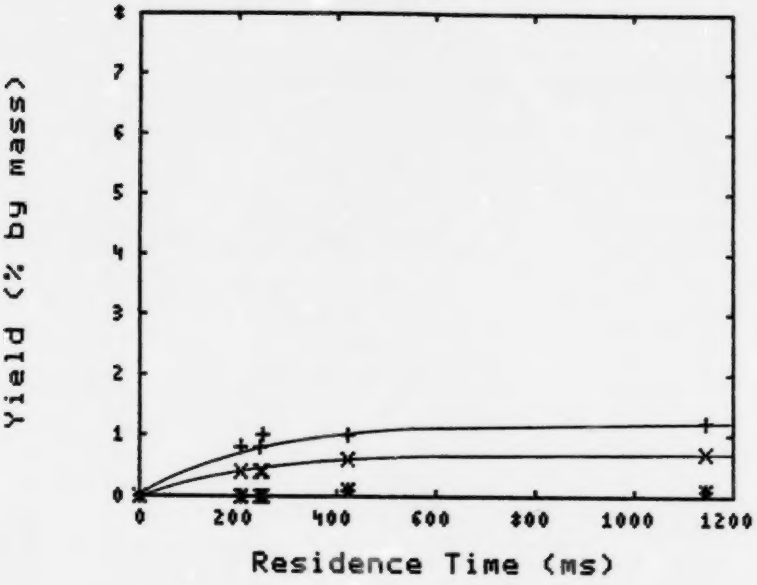

Figure 14.6.9 Fast Pyrolysis of Red Maple (650 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

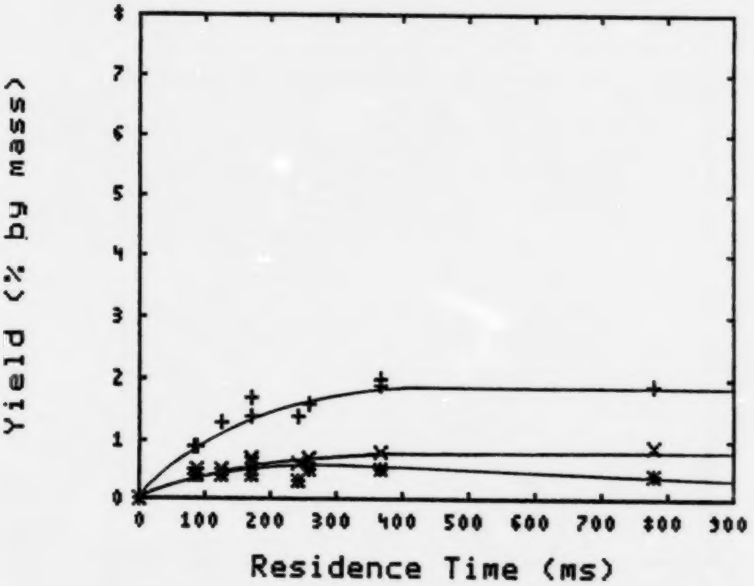

Figure 14.6.10 Fast Pyrolysis of Red Maple (700 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

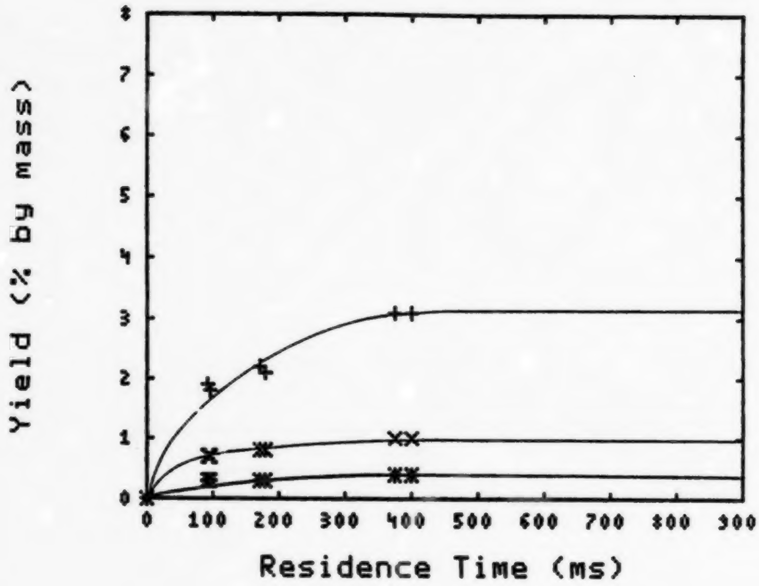

Figure 14.6.11 Fast Pyrolysis of Red Maple (750 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

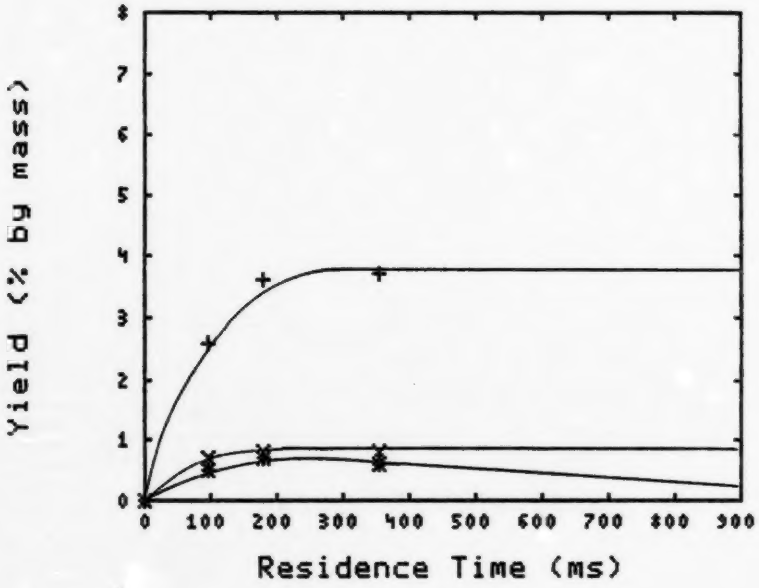

Figure 14.6.12 Fast Pyrolysis of Red Maple (800 C): Ethylene (+), Propylene (X) and Acetylene (*) Yields vs Residence Time.

14.7 Computer Kinetic Analysis of the Water-Gas Shift Reaction

```
CO2 CONCENTRATION VS TIME AT 850 C
__________________________________

EXPERIMENT I.D.: WG-12
[CO2]o = 6.44E-04 molar
[H2]o = 3.14E-03 molar

 [CO2]                  TIME
 (molar)                 (s)
______________________________

 6.44E-04              0
 6.118E-04             104.0465
 5.796E-04             214.2897
 5.474E-04             331.4477
 5.152E-04             456.3698
 4.83E-04              590.07
 4.508E-04             733.7729
 4.186E-04             888.976
 3.864E-04             1057.5372
 3.542E-04             1241.8007
 3.22E-04              1444.7828
 2.898E-04             1670.4559
 2.576E-04             1924.201
 2.254E-04             2213.5629
 1.932E-04             2549.5925
 1.61E-04              2949.4238
 1.288E-04             3441.7628
 9.66000003E-05        4080.4257
 6.44000002E-05        4986.2348
 3.22000002E-05        6544.7307
```

```
CO2 CONCENTRATION VS TIME AT 900 C
__________________________________

EXPERIMENT I.D.: WG-7
[CO2]o = 5.47E-04 molar
[H2]o = 2.67E-03 molar

 [CO2]                  TIME
 (molar)                 (s)
______________________________

 5.47E-04              0
 5.1965E-04            26.2484
 4.923E-04             54.06
 4.6495E-04            83.6159
 4.376E-04             115.1302
 4.1025E-04            148.8588
 3.829E-04             185.1105
 3.5555E-04            224.2632
 3.282E-04             266.7853
 3.0085E-04            313.2683
 2.735E-04             364.473
 2.4615E-04            421.4013
 2.188E-04             485.4107
 1.9145E-04            558.4041
 1.641E-04             643.1691
 1.3675E-04            744.0276
 1.094E-04             868.2205
 8.20499997E-05        1029.3223
 5.46999997E-05        1257.8094
 2.73499997E-05        1650.9311
```

14.7 Sample Results of the Computer Kinetic Analysis of the Water-Gas Shift Reaction.

14.8 Arrhenius Plots for the Product Gases from Cellulose

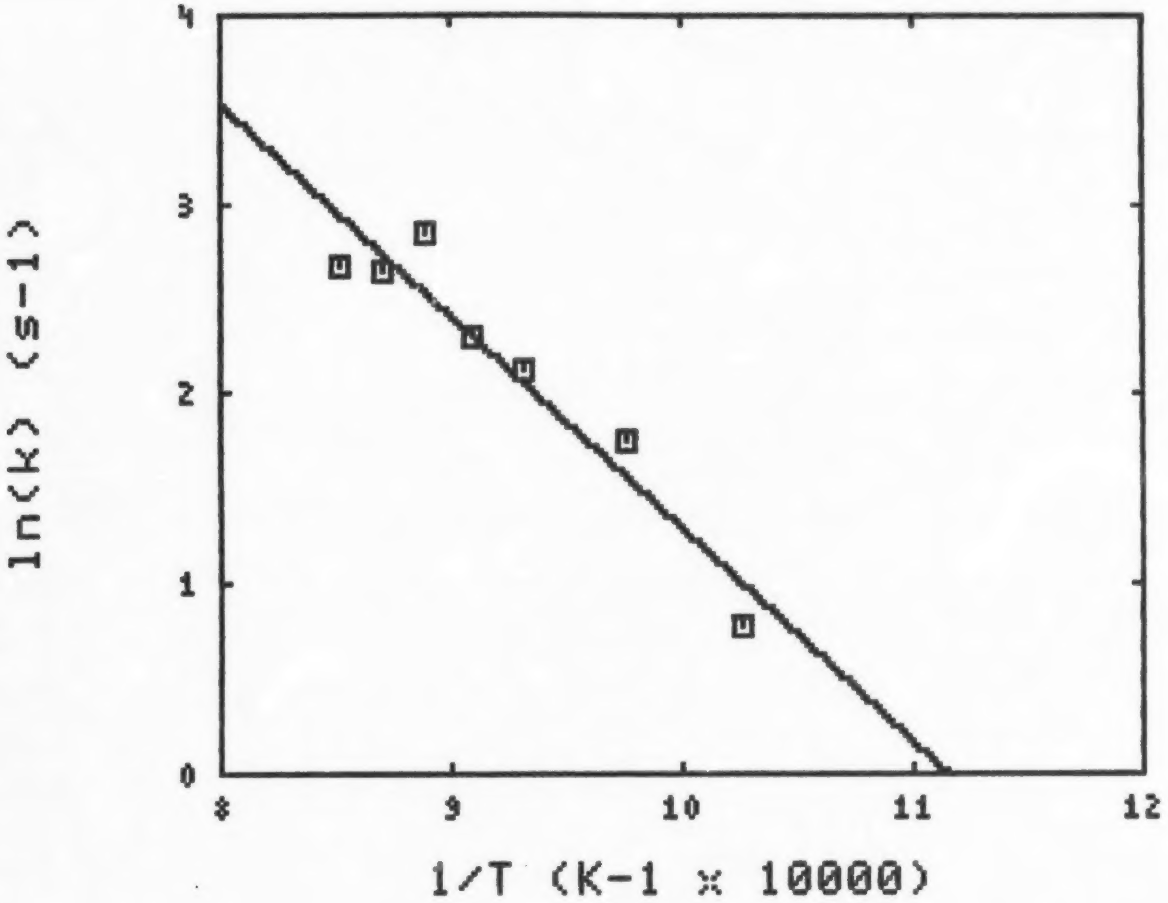

FIGURE 14.8.1. Arrhenius Plot for Hydrogen Production from Cellulose

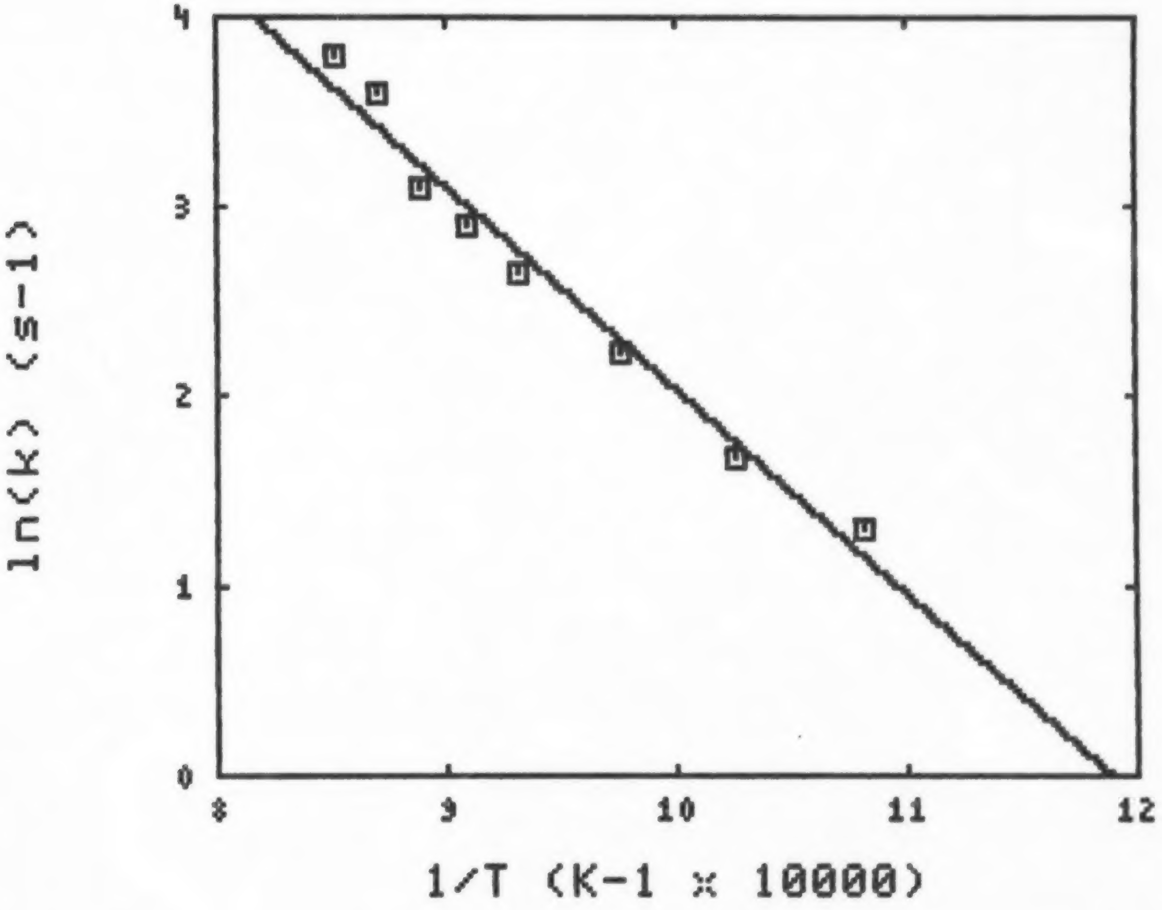

FIGURE 14.8.2. Arrhenius Plot for Carbon Monoxide Production from Cellulose

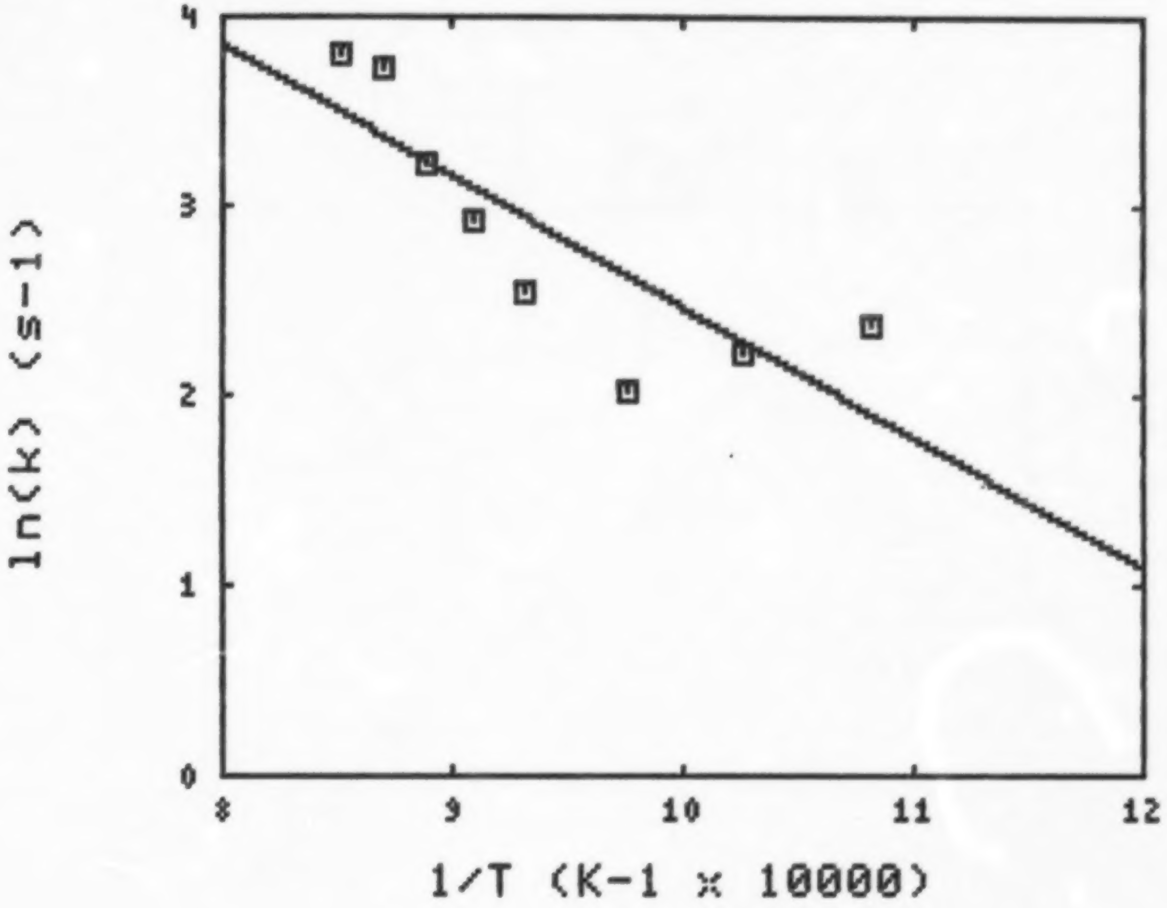

FIGURE 14.8.3. Arrhenius Plot for Carbon Dioxide Production from Cellulose

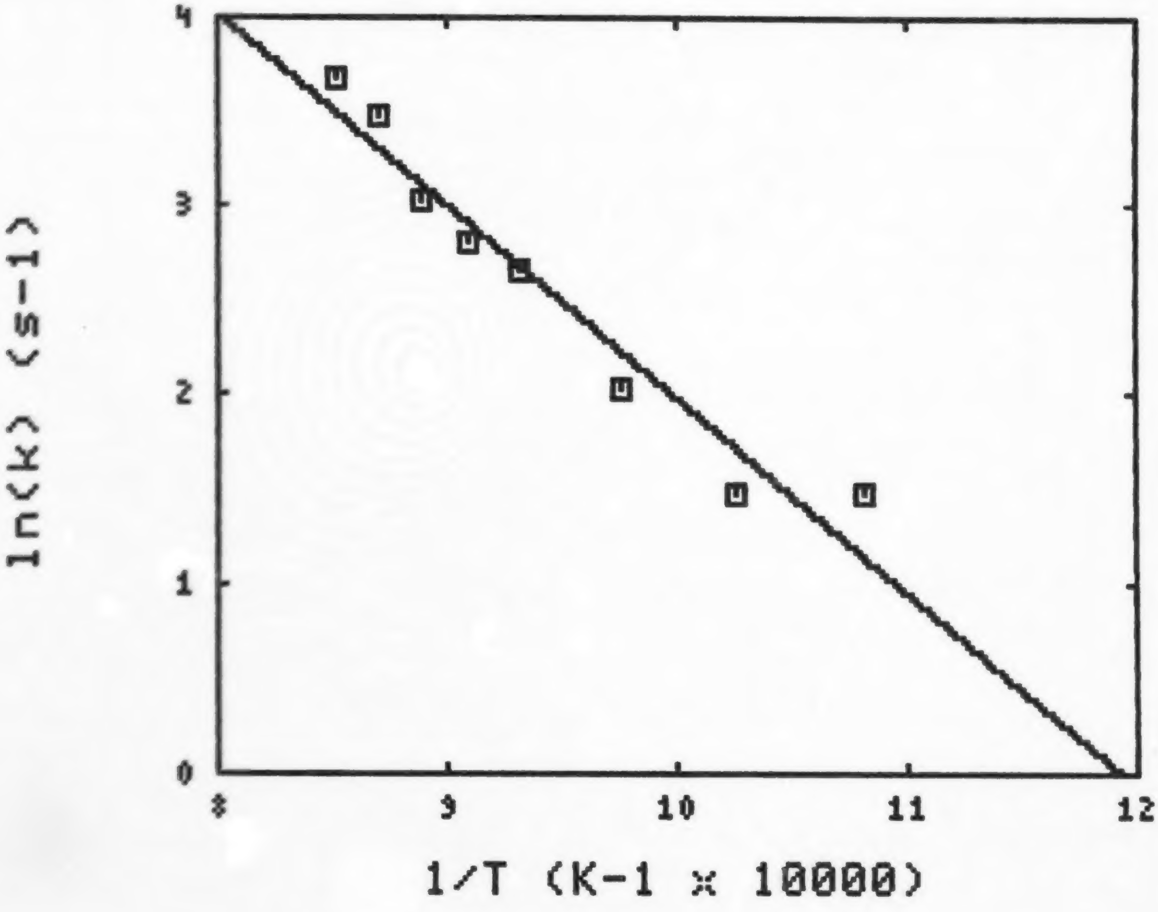

FIGURE 14.8.4. Arrhenius Plot for Ethylene Production from Cellulose

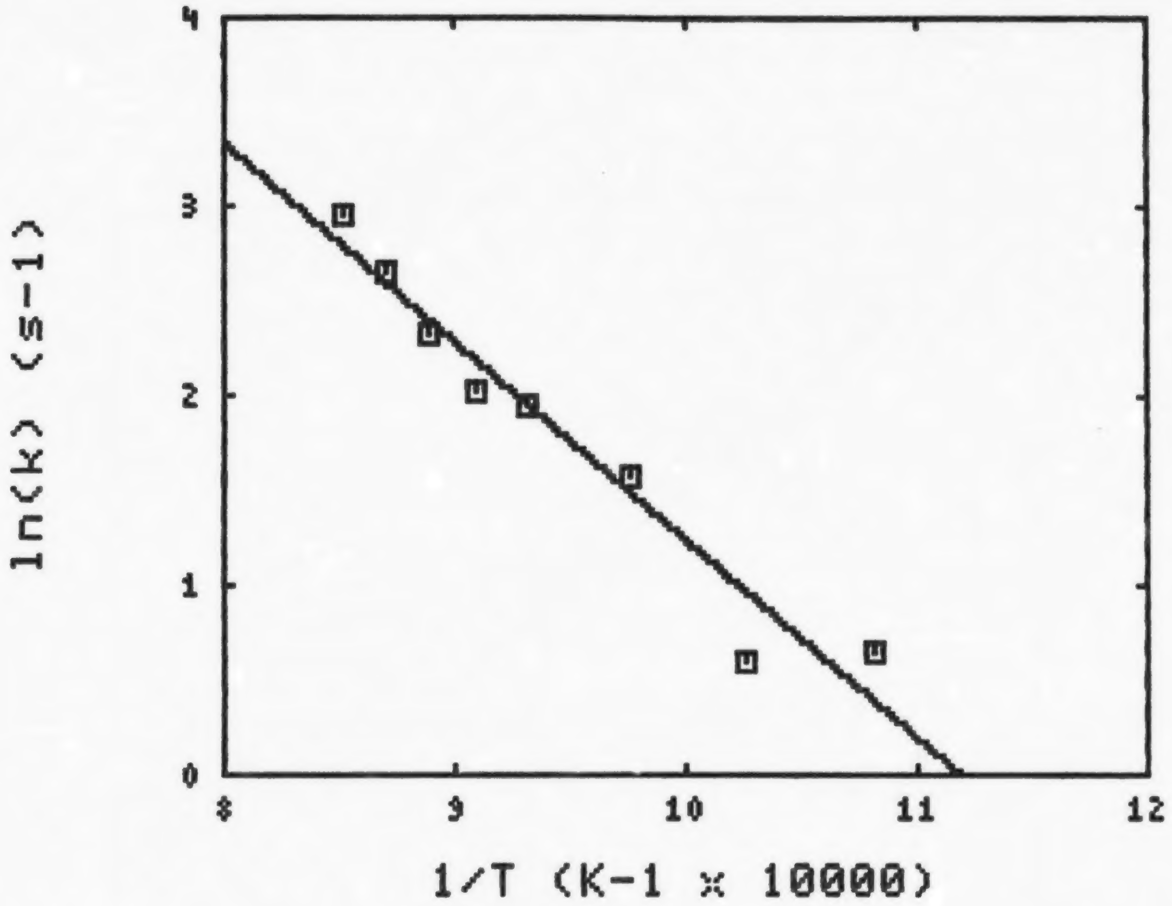

FIGURE 14.8.5. Arrhenius Plot for Methane Production from Cellulose

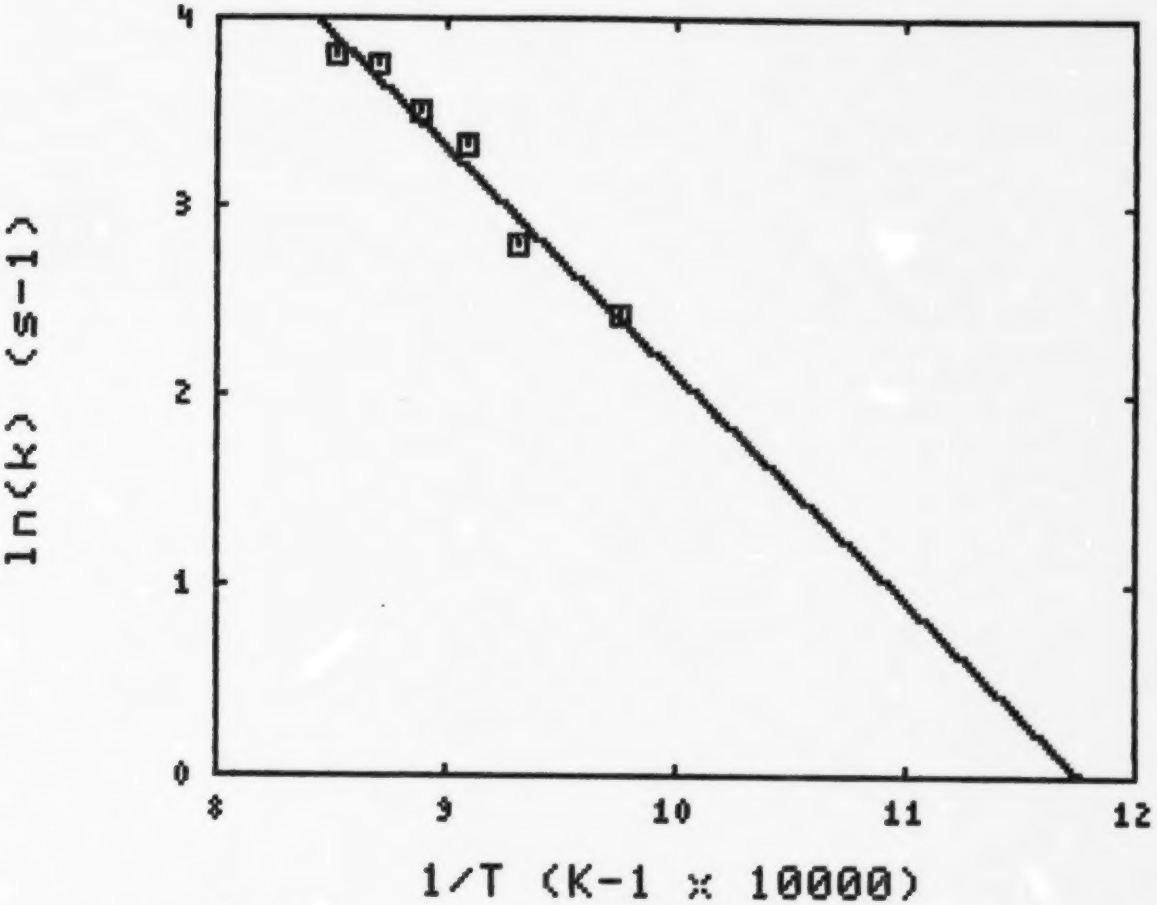

FIGURE 14.8.6. Arrhenius Plot for Acetylene Production from Cellulose